The Relation of the Changes in Reactivity of Dried Cellulose to the Temperatures of Cellulose Wetting-Drying History

by

Theodore Peng-Jung Yin, B.Sc.

For Reference

NOT TO BE TAKEN FROM THIS ROOM

Ex libris
universitatis
albertaensis

UNIVERSITY OF ALBERTA
QUAECUMQUE VERA

Digitized by the Internet Archive
in 2018 with funding from
University of Alberta Libraries

https://archive.org/details/Yin1957

UNIVERSITY OF ALBERTA

SCHOOL OF GRADUATE STUDIES

The undersigned hereby certify that they have read and recommend to the School of Graduate Studies for acceptance, a thesis entitled "The Relation of the Changes in Reactivity of Dried Cellulose to the Temperatures of Cellulose Wetting - Drying History" submitted by Theodore Peng - Jung Yin, B. Sc., in partial fulfilment of the requirements for the degree of Master of Science.

PROFESSOR.

PROFESSOR.

PROFESSOR.

Date..April 15/57....

ABSTRACT

This project is a continuation of the studies on the reactivity of cellulose alternately wetted and dried, with special emphasis on its relation to the wetting temperatures. It is also aimed to reveal the manner in which the substituents are distributed at the primary and secondary hydroxyls of the anhydroglucose units.

Dewaxed cotton linters were subjected to wetting and drying processes for as much as fifteen times, at different wetting temperatures of 0°, 25°, 50± 5°, 75± 5° and in steam. The samples, which had been thoroughly dried over phosphorus anhydride in vacuum and stored in desiccators over the mentioned drying agent were then subjected to the following reactions:

1. Nitration in technical nitrating mixture.
2. Lead tetraacetate oxidation of the cellulose nitrate.
3. Tosylation followed by iodination of the pretreated native cellulose.

The nitration data for 0° and 25° wetting series show a gradual increase in their degree of substitution with the increase of wetting and drying cycles, while the findings for 50°, 75° and steam series exhibit an opposite trend. The oxidation results correlate with the nitration data with the exception of 25° wetting series. With the aid of mathematical treatment, a certain type of distribution of the nitro groups at primary and secondary positions is suggested.

Tosylation and iodination reactions reveal a

gradual decline in reactivities for the 25° series for both the primary and secondary hydroxyls with the increase of wetting cycles. For samples wetted only once at different temperatures, the accessibilities at the two positions (primary and secondary) seem to reach a maxiumum between the temperature range 25° - 75°.

The result as a whole supports the hypothesis that the previous moisture history plays an important role to influence the reactivities of the cotton linters.

hesis
957
25

THE UNIVERSITY OF ALBERTA

THE RELATION OF THE CHANGES IN REACTIVITY OF DRIED CELLULOSE TO THE TEMPERATURES OF CELLULOSE WETTING-DRYING HISTORY

A DISSERTATION
SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

by

THEODORE PENG-JUNC YIN, B. Sc.

EDMONTON, ALBERTA

April 1957

ACKNOWLEDGEMENTS

The author wishes to express his sincere thanks and appreciation to Dr. Robert K. Brown for his most helpful advice and assistance throughout the entire period of this research project.

Grateful acknowledgement is also extended to the Shell Oil Company of Canada and the National Research Council of Canada for their financial assistances which enabled the author to continue with his studies.

He is also indebted to the members of the staff of the Department of Chemistry of the University of Hong Kong and the Department of Chemistry of the University of Alberta who have taught him, and given him inspiration to continue with further studies in chemistry.

TABLE OF CONTENTS

Page

Introduction 1

Experimental

1. Preparations of Cellulose Samples
   A. Swelling of Cellulose Samples in Distilled Water at 25 ± 0.1° 21
   B. Swelling of Cellulose Samples in Distilled Water at 50 ± 5° 26
   C. Swelling of Cellulose Samples in Distilled Water at 75 ± 5° 27
   D. Swelling of Cellulose Samples in Ice-Distilled Water Mixture 27
   E. Swelling of Cellulose Samples in Steam 28
   F. Preparation of Chemically Reactive Cellulose 31
   G. Swelling of Cellulose Samples at Different Temperatures 32
2. Nitrations with Sulfuric Acid-Nitric Acid Mixture 33
3. Determinations of Nitrogen Content
   A. Corrections for Moisture Absorption 35
   B. Analyses of Nitrogen by Du Pont Semi-Micro Nitrometer 35
4. Oxidations of Nitrocelluloses with Lead Tetraacetate 41
5. Esterifications with p-Toluenesulfonyl Chloride
   A. Tosylations of Cotton Linters 52
   B. Iodinations of Tosylated Cellulose 54
   C. Sulfur Analyses - Parr Bomb Method 55
   D. Iodine Analyses - Clark Method 58

Page

Results and Discussion

1. Nitrations of Series T 61

2. Consumptions of Lead Tetraacetate by Cellulose Nitrates Series T 66

3. Distributions of Nitro Groups at Primary and Secondary Positions of the Anhydroglucose Units (Based on Three Possible Modes of Nitration) 83

4. Tosylations and Iodinations Data of Series I, II and DT 98

Distributions of Tosyl Groups at Primary and Secondary Positions of the Anhydroglucose Units

5. Comparison of the Data Obtained from Nitration and Tosylation - Iodination Reactions 107

Bibliography 116

LIST OF TABLES

Page

Table

1. Wetting Cycles of Cotton Linters in Distilled Water at 25 ± 0.1°C 23-5
2. Wetting Cycles of Cotton Linters in Distilled Water at 50 ± 5°C 26
3. Wetting Cycles of Cotton Linters in Distilled Water at 75 ± 5°C 27
4. Wetting Cycles of Cotton Linters in Ice-Distilled Water Mixture 29
5. Wetting Cycles of Cotton Linters in Steam 30
6. Cotton Linters Wetted Once at Different Temperatures 32
7. Nitrogen Contents of Nitrocellulose Samples Series T Expressed in %N by Weight 63
8. Nitrogen Contents of Nitrocellulose samples Series T Expressed as Total Number of Hydroxyls Substituted 64
9. Lead Tetraacetate Oxidations of Cellulose Nitrate (Zero Wetting Sample) 46
10. Lead Tetraacetate Oxidations of Cellulose Nitrates (T-0 Samples) 47
11. Lead Tetraacetate Oxidations of Cellulose Nitrates (T-25 Samples) 48
12. Lead Tetraacetate Oxidations of Cellulose Nitrates (T-50 Samples) 49
13. Lead Tetraacetate Oxidations of Cellulose Nitrates (T-75 Samples) 50
14. Lead Tetraacetate Oxidations of Cellulose Nitrates (T-S Samples) 51

Page

15. Consumptions of Lead Tetraacetate Oxidations of the Nitrocellulose Samples Series T 69

16. Total Number of Free Hydroxyls in the Cellulose Nitrates of Series T 87

17. Number of Free Secondary Hydroxyls as Glycols in the Cellulose Nitrates of Series T 87

18. Total Number of Free Secondary Hydroxyls of Series T based on Theory of Random Distribution 88

19. Total Number of Free Secondary Hydroxyls of Series T based on Theory of Depression 88

20. Total Number of Free Secondary Hydroxyls of Series T based on Theory of Heterogeneous Substitution 88

21. Number of Free Primary Hydroxyls of Series T based on Theory of Random Distribution 89

22. Number of Free Primary Hydroxyls of Series T based on Theory of Depression 89

23. Number of Free Primary Hydroxyls of Series T based on Theory of Heterogeneous Substitution 89

24. Number of Primary Hydroxyls Nitrated of Series T based on Theory of Random Distribution 90

25. Total Number of Secondary Hydroxyls Nitrated of Series T based on Theory of Random Distribution 90

26. Number of Primary Hydroxyls Nitrated of Series T based on Theory of Depression 91

27. Total Number of Secondary Hydroxyls Nitrated of Series T Based on Theory of Depression 91

28. Number of Primary Hydroxyls Nitrated of Series T based on Theory of Heterogeneous Substitution 92

29. Total Number of Secondary Hydroxyls Nitrated of 92

Page

Series T based on Theory of Heterogeneous Substitution

30. Tosylation of Cellulose Samples Series I 100

31. Tosylation of Cellulose Samples Series II 101

32. Combined Tosylation and Iodination Data of Series I 103

33. Combined Tosylation and Iodination Data of Series II 104

34. Tosylation of Cellulose Samples Series DT 108

35. Combined Tosylation and Iodination Data of Series DT 109

36. Comparison of Nitration and Tosylation - Iodination Data with Respect to Wetting Cycles at 25° 111

37. Comparison of Nitration and Tosylation - Iodination Data with Respect to Wetting Temperatures 112

LIST OF FIGURES

Page

Figure

1. Plane projection of cellulose chain of glucose units 3
2. Schematic representation of cellulose structure 3
3. Unit cell of crystalline cellulose 6
4. Du Pont semi-micro nitrometer (hand shaken model) 37
5. Amperometric titration apparatus for lead tetraacetate oxidation 44
6. Sample titration graph using amperometric method 44
7. Nitrogen contents in % by weight of the nitrocellulose samples series T 67
8. Lead tetraacetate oxidations of cellulose nitrate in ethyl acetate-acetic acid (zero wetting sample) 71
9. Lead tetraacetate oxidations of cellulose nitrates in ethyl acetate-acetic acid (T-0 samples) 72-3
10. Lead tetraacetate oxidations of cellulose nitrates in ethyl acetate-acetic acid (T-25 samples) 74-5
11. Lead tetraacetate oxidations of cellulose nitrates in ethyl acetate-acetic acid (T-50 samples) 76
12. Lead tetraacetate oxidations of cellulose nitrates in ethyl acetate-acetic acid (T-75 samples) 77
13. Lead tetraacetate oxidations of cellulose nitrates in ethyl acetate-acetic acid (T-S samples) 78-9
14. A summary on the consumptions of lead tetraacetate by nitrocellulose samples series T 82
15. Number of primary hydroxyls nitrated of the nitrocellulose samples series T based on theory of random distribution. 95

Page

16. Total number of secondary hydroxyls nitrated of the nitrocellulose samples series T based on theory of random distribution 96

17. Comparison of number of primary and secondary hydroxyls substituted from nitration and tosylation-iodination data with respect to wetting cycles at 25° 113

18. Comparison of number of primary and secondary hydroxyls substituted from nitration and tosylation-iodination data with respect to wetting temperatures 114

INTRODUCTION

The modification of the properties of cotton linters brought about by alternate wetting and drying cycles have been studied by Rosenthal and Brown (1) and Brickman, et al (2). The changes in reactivities were revealed by measurements of accessibility to thallous ethylate, of degree of nitration, viscosity determinations and lead tetraacetate oxidation of the nitrates. as well as by data on the water sorption and heats of wetting of the pretreated native cellulose samples.

The purpose of the present project as outlined in this thesis was to confirm some of these findings, to study the relation between the modification in reactivities and the wetting temperatures, and to reveal the relative changes in accessibilities of the primary and secondary hydroxyls in the anhydroglucose units by the alternate wetting and drying process. The following reactions: nitration, lead tetraacetate oxidation of the nitrates, and tosylation followed by iodination, were employed in these studies.

The importance of cellulose chemistry cannot be overemphasized. Cellulose is the most abundant naturally occurring organic compound. The understanding of its chemistry might reveal the secrets of other natural and synthetic polymers. Thus it is of both practical and theoretical interest.

Technically speaking, 'cellulose' denotes the residues obtained by subjecting vegetable material to certain pulping processes (5). The purest form of raw cellulose is obtained from two types of hair found on cotton seed, namely, cotton and cotton linters. The former is used chiefly in the textile industry, whereas cotton linters find their greatest value in the preparation of chemical cellulose, which is subsequently employed for the manufacture of such common products as nitrocellulose, rayon and cellulose xanthates.

In the chemical sense, cellulose is a polysaccharide of sufficient chain length to be insoluble in water or dilute acids and alkalies at ordinary temperatures. It consists of anhydroglucose units linked together through the 1 and 4 carbon atoms with a β-glucosidic linkage (Fig. 1), and gives a typical x-ray diagram. Although cellulose does not contain macromolecules all of the same length, upon complete hydrolysis it yields only D-glucose. The term 'degree of polymerization (D.P.)' represents an average value for the number of glucose anhydride units in any given sample. The average D.P. of cotton is 2020, whereas that of cotton linters is 1440 (5). In partially hydrolysed cellulose the D.P. may drop into the range of 50-500 and still retain the characteristics of the cellulose polymer.

Modern theories regarding the physical structure of cellulose fibers indicate that, on the x-ray scale, it consists of a continuous network of crystalline and inter-

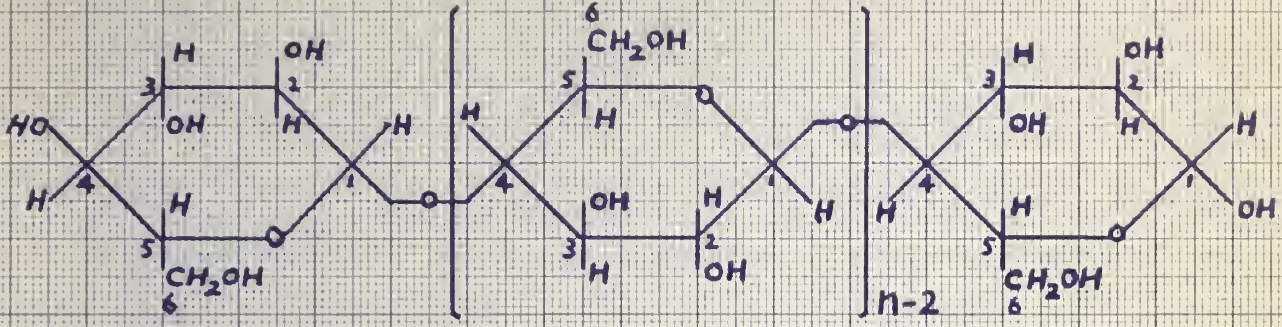


Fig. 1 Plane projection of cellulose
Chain of glucose units

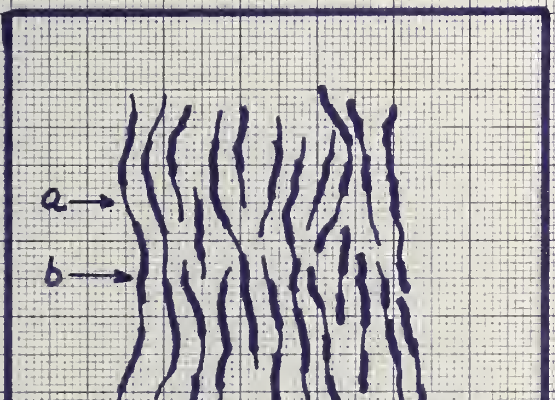


Fig. 2 Schematic representation of
cellulose structure
a: amorphous region
b: crystalline region

crystalline localities through which the long macromolecular main valence chains of glucose units persist. The crystalline sections are believed to be those regions where portions of several primary valence chains are sufficiently close together and in sufficient alignment to allow crystallization forces to produce a definite lattice, whose outer edges are somewhat irregular. From these 'crystallites' the cellulose chains continue into intercrystalline or amorphous sections of more or less disorganized formation, which have no regular crystalline pattern (Fig. 2). The tenacity and strength of the cellulose is located in the crystalline structure whereas the elasticity and extensibility is due to amorphous regions.

By a differential 'hydrolytic' method of analysis, Nickerson and Habrle (6) found that, in purified cotton fibers, cellulose appeared to exist in three distinguishable states of organization. The three states, amorphous, mesomorphous, and crystalline are present in amounts of 3%, 3%, and 94%, respectively. The amorphous (most disordered) component appears to hydrolyze very easily and to have relatively high moisture affinity in comparison with the rest of the structure. Mesomorphous or transitional cellulose hydrolyses less readily and seems to be more heterogeneous. The crystalline component exhibits high and uniform resistance to hydrolysis. In hygroscopic and hydrolytic behavior the latter two states bear a closer

resemblance to each other than to the amorphous component.

Berkley and Kerr (7), however, showed that the x-ray patterns of undried cotton fibers taken from the developing bolls indicated little or no evidence of the crystalline cellulose. The pattern of native cellulose appeared only at the time when the fibers underwent their initial dehydration. This was explained by the assumption that in the living boll, the hydroxyls on adjacent chains are separated by water molecules. The type of hydrogen bonding associated with crystalline cellulose apparently did not occur until a certain portion of the water was removed.

The unit cell dimensions of the crystalline cellulose have been postulated by Meyer and coworkers (8) as shown in Fig. 3. Each unit cell contains four glucose residues. The nature of the forces which hold the lattice structure together has been reviewed by Mark (9). In the direction of the 'b' axis the glucose units are held together by strong 1, 4 - glucosidic primary valence bonds. Along the 'a' axis the glucose rings are separated by only 2.5 Å. This suggests that relatively strong forces are acting in this plane, and it is reasonable to assume that hydrogen bonds are formed between oxygen atoms of adjacent molecules. Along the 'c' axis the nearest distance between atomic centers is 3.1 Å, which corresponds closely to the distance expected if van der Waals forces hold the lattice together in this direction. Thus, cellulose may be regarded as a combination of a chain lattice and

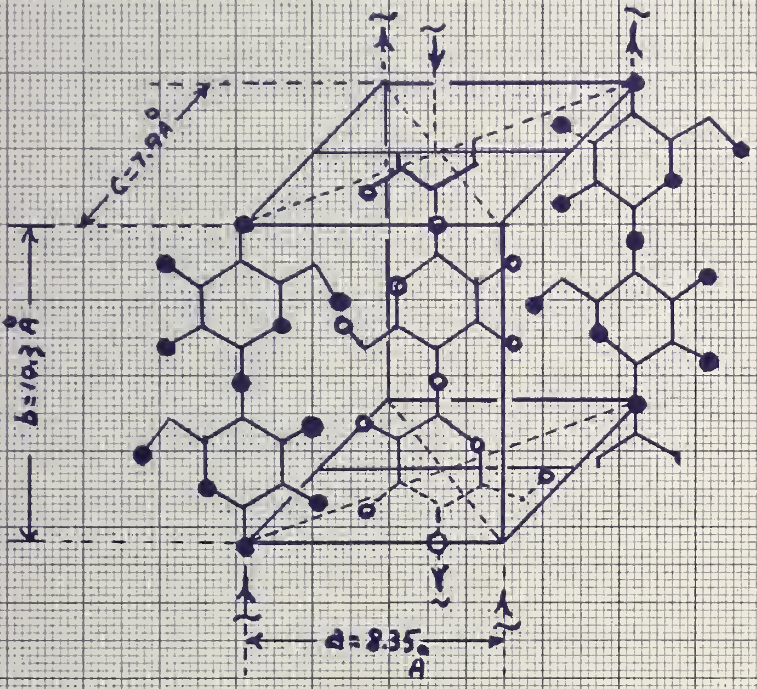


Fig. 3 Unit cell of crystalline cellulose

HUGHES OWENS 315W-METRIC

a layer lattice composed of primary valence forces along the 'b' axis, relatively strong hydrogen bond network in the 'ab' plane, and weaker van der Waals forces perpendicular to the 'ab' plane. These three different forces acting in three different directions may be responsible in part for many of the properties of cellulose in the solid state.

The physcial structure of cellulose as outlined will be affected, to some extent, by the presence of water. One of the most pronounced visible roles of water is its swelling effect upon either unpurified or purified cellulose.

On the basis of x-ray diagrams of swollen cellulose, Katz (10) defined two principal types of swelling, namely, 'intercrystalline' and 'intracrystalline'. In the former type, the liquid penetrates only the amorphous region; whereas in intracrystalline swelling, both the interior of the crystalline and the intercrystalline portions are affected. This can be achieved by soaking cellulose in aqueous solution of concentrated caustic soda. Prior to the time when heavy water became an analytical tool for the elucidation of reactions and structures, it was commonly believed that ordinary water was capable of producing only intercrystalline swelling, being unable to penetrate the crystalline portion of cellulose. Champetier and Viallard (11) indicated that cellulose reacts quantitatively with heavy water, such that the three hydrogen atoms of the hydroxyl groups in every glucose residue

are slowly replaced by deuterium. Frilette, Hanle and Mark (12) also observed that heavy water penetrated the whole mass of cellulose, including the crystallites, and suggested that ordinary water must do so likewise. More recently, Legrand and Champetier (13) investigated the hydration of cellulose by x-ray diffraction; they concluded that the crystal lattice of all forms of cellulose is accessible to water.

As a general rule, any liquid or vapor which causes swelling must be capable of breaking the secondary valence bonds between macromolecules and of forming their own bonds with the polymer. Cellulose swollen with water shows an increase in volume of the solid though the total volume is less than that of the original solid plus liquid. This is due to the compression of water and cellulose molecules caused by the attraction of the water molecules by hydroxyl groups in cellulose. Organic liquids, in general, swell cellulose to some lesser extent, the swelling being chiefly dependent on the polarity and molecular volume of the liquid. Thus, methanol swells cellulose less than does water; with increasing molecular weight the swelling by normal alcohols decreases until it becomes negligible in n-butanol.

The great affinity of dry cellulose for water is attributed to the hydrogen bonding capacity of the hydroxyl groups because progressive masking of the latter by esterification reduces the amount of moisture absorbed from standard, humid surroundings (14). The sorption of water seems to take place in three stages (15). The first step is due to the strong hydrogen bonding of single molecules

of water to all of the hydroxyls accessible in the amorphous portion. The intermediate stage corresponds to the filling up of the finer capillaries. In the final adsorption, cellulose swells and there is condensation of free or unbound water in the coarser capillaries.

Schur and Hoos (16) found that cellulose, which has been shredded in the presence of water, subsequently dried, and then nitrated, gave nitrates with higher nitrogen content than similar cellulose which has been shredded in the dry state and then nitrated. An increase in the accessible cellulose can also be brought about by the industrial procedure of beating pulps (17). Even the simple action of combing the cotton fibers is said to cause an increase in the amount of "ordered cellulose".

On the other hand, the action of light will cause photo-oxidation of the cellulose chain (18). DeCroes and Tamblyn also showed that cellulose esters suffer decomposition under prolonged action of heat and light (19).

It is quite obvious, therefore, that the growing conditions affecting the plant, the presence or absence of water in contact with the cellulosic material during its manufacture, the mechanical manipulation and the storage of the raw material, all play an important role in the determination of the physical structure and chemical reactivity of cellulose. In order to produce a vigorously uniform product, the raw materials must be carefully screened and the processes should be rigidly standardized.

As previously outlined, this project was undertaken in an attempt to investigate more fully the role of water in affecting the properties of cellulose. In order to magnify the swelling effects the cellulose was alternately wetted, vigorously dried, re-wetted and redried for as many as fifteen cycles. Since the wetting temperature will inevitably influence the accessibility to some extent, samples were soaked in water at five different temperatures for the studies.

The changes in the reactivity of cellulose, caused by pre-treatment of the samples with swelling agents, reveal themselves in the properties of their derivatives (4, 20). Furthermore, the manner of distribution of substituents on the hydroxyl groups of the glucose units causes changes in viscosities and solubilities in different solvents, properties of which are of considerable concern in industrial application of the cellulose derivatives.

Nitrocellulose is one of the most important derivatives of cellulose, being produced in enormous quantities annually by industries. It can be prepared in a number of different ways. With a mixture of nitric acid and phosphorus pentoxide, cellulose can be nitrated to a nitrogen content close to the theoretical 14.17% trinitrate (21). Nitration with glacial acetic acid, acetic anhydride and nitric acid yields nitrocellulose with 14.08% N (22). However, a nitric acid and phosphoric acid mixture gives a much lower degree of nitration.

The most commonly used nitrating agent is a mixture of nitric acid and sulphuric acid, giving nitrates with nitrogen content up to 13.7% (23).

Although cellulose can be nitrated with concentrated nitric acid alone, nitration is, in practice, always achieved by the use of a mixture of nitric acid and sulphuric acid. The nitrogen content of the products obtained depends upon the amount of water present in the reaction mixture. Technical nitration mixtures can be made up according to the table assembled by Dorée (23) to yield nitrated celluloses of 6.50 to 13.65% N. The theoretical nitrogen contents of the mono, di and trinitrate are 6.77%, 11.13%, and 14.17% respectively. The highest is obtained with a system represented by $HNO_3 + n(H_2SO_4 \cdot H_2O)$, and the lowest when nitric acid is present as a hydrate, $HNO_3 \cdot H_2O$. The sulphuric acid appears, therefore, in one of its functions to act as a dehydrating agent for the nitric acid.

According to evidence presented by Berl and co-workers (22), cellulose nitration involves the usual principle of esterification with a reversible mechanism; that is, when molecular quantities of an acid and an alcohol react, an ester is formed and water is produced. The reaction is forced to completion with an excess of nitric acid. Therefore the equilibrium (or the N content of the product) is determined by the final composition of the nitrating solution rather than by the composition

of the original acid mixture.

The rate of nitration of cellulose increases with rise in temperature, but degradation of the cellulose molecule also increases. Schur and Hoos (16) stated that esterification, oxidation and hydrolysis may take place to a greater or lesser extent, according to the composition of the nitrating mixture, the ratio of liquid to the cellulose, the temperature, the intensity of agitation and the physical condition of the cellulose. As nitration proceeds, water and heat are generated, and nitric acid is consumed. If the reaction proceeds too rapidly, the acid immediately adjacent to the fiber or within it, may grow so rich in water and so poor in nitric acid that hydrolysis is promoted. In addition, localized generation of heat may lead to oxidation and to hydrolysis of the cellulose. It is obvious that these actions will bring forth a heterogeneous nitration product. This indicates the necessity of standardizing carefully all the conditions in the nitration procedures.

In the laboratory, uniform products are obtained by nitrating small batches of cellulose (approximately 1.5 gram), by carefully controlling the ratio of cellulose to acid mixture, by keeping the nitration time and temperature constant and by stirring the reactants throughout the period. The crude nitrate is contaminated with nitrating acid, sulphuric acid esters of the cellulose and nitro compounds produced from the impurities found in the fibers. These impurities, which would render the product liable to

spontaneous decomposition, are removed by adequate washing and the cellulose nitrate is subsequently stabilized by boiling with a water - ethanol solution.

A du Pont semi-micro nitrometer (24) provides an accurate and relatively simple method of nitrogen estimation. The nitrogen content is calculated from the volume of nitric oxide liberated on the reaction of the nitrocellulose with concentrated sulfuric acid in the presence of mercury.

$$\text{Cellulose} - ONO_2 + H_2SO_4 + Hg \longrightarrow \text{Cellulose} + NO + H_2O + HgSO_4$$

As shown in Figure 1, there are two kinds of hydroxyl groups present in each anhydroglucose unit, namely primary and secondary. The former is located on carbon six, and the latter exists as a trans glycol unit on carbons two and three. Any analytical tool that could disclose the mode of substitution at the hydroxyls by nitro groups might help to reveal the mechanism of the nitration reaction.

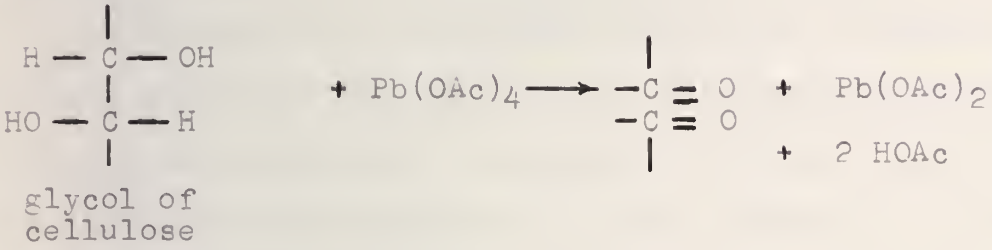
Some work has been done on partially acetylated cellulose by the use of tosylation and iodination method (25) to study the reactivity of the primary and secondary hydroxyls. However within the author's knowledge, no report in the literature deals with the application of this technique to cellulose nitrates. Although Murray and Purves (26) once attempted to employ iodination reaction alone to estimate the number of primary positions nitrated, their findings indicated a sizeable loss of nitro groups during iodination. Thus the method seems unsuitable in our purpose since we are measuring the small differences

in degree of nitration caused by different wetting cycles and temperatures.

Lead tetraacetate, on the other hand, preferentially cleaves unesterified glycol groups and has been employed successfully to determine what fraction of the total hydroxyls exists as free glycol units. Hockett, Cramer and Purves oxidized commercial acetone-soluble cellulose acetates with lead tetraacetate and found that distribution of hydroxyls on a partially acylated cellulose was largely a matter of chance (27). The same reagent was also used by Mahoney and Purves (28) on partially etherified cellulose to determine the mode of etherification. They reported that the distribution of free glycol groups in the cellulose ethers depends, to a certain degree, on the mode of preparation. Brown (29) oxidized commercial cellulose nitrates with lead tetraacetate to small but variable extents. He found that wetting and redrying of highly swollen linters prior to technical nitration increased the level of oxidation. In a repetition of this work, employing improved techniques, cellulose nitrates of varying nitrogen content were oxidized with lead tetraacetate in order to gain some information concerning the manner of substitution in the anhydroglucose units of cellulose.

The mechanism of glycol cleavage by lead tetraacetate has been presented by Heidt, Gladding and Purves (30). Oxidation will take place only when both hydroxyl groups of the glycol in the cellulose are in free unesterified or unetherified state. Lead tetraacetate condenses with glycols

to form an unstable cyclic ester with lead as its central atom. The valence of the central atom is then immediately reduced by two units with the production of acetic acid and lead acetate. The overall reaction can be represented as follows:



Thus one mole of lead tetraacetate is required to split one glycol group in one anhydroglucose unit. By plotting the consumption of oxidant against time, the point at which the curve begins to show zero slope would indicate the completion of oxidation. The height of the ordinate, at zero slope of the curve, should therefore represent the total consumption of the oxidant by the cellulose nitrate.

The course of oxidation is usually followed by removing, at suitable intervals, aliquots of the oxidizing mixture. The excess of oxidant is then titrated with standard sodium thiosulphate solution (3). The oxidation-reduction system involved is a familiar one.

$$Pb(OAc)_4 + 2\ KI \longrightarrow Pb(OAc)_2 + I_2 + 2\ KOAc$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2\ NaI$$

Starch end point was used by Rosenthal (31) who encountered some difficulties with the recurrance of light blue color after the titrated mixture had been standing for awhile. This might be predicted since the titrating mixture is composed of both organic and inorganic layers. In order

to overcome this uncertainty, an amperometric titration method was employed in the present investigation. With a rotating platinum electrode operating at a reasonable speed, the mixture being titrated appeared to be well dispersed and the end point was more accurate.

A method of esterifying cellulose, in addition to those involving free acids (e.g. nitric acid) and acid anhydride (e.g. acetic anhydride) is by the use of acid chlorides in the presence of either alkali or a tertiary organic base. Much published work of derivatives thus obtained has been concerned with esters of p-toluenesulfonic acid (32). The degree of esterification for a single treatment corresponds to somewhat less than a mono ester, although Rigby (33) once reported the reaction of p-toluenesulfonyl chloride (tosyl chloride) on alkali cellulose, employing first a temperature not above 20°, then an elevated temperature up to 50°, to produce esters possessing 1.5 to 1.7 tosyl groups per glucose unit.

In recent years tosylation has been used as a tool in studying the distribution of substituents in cellulose derivatives. The primary and secondary hydroxyl groups can be distinguished by the relatively selective reaction of sodium iodide in acetone solution, which replaces selectively with iodine those tosyl groups on primary hydroxyls (34). Cramer and Purves (25) employed tosylation to differentiate the relative rates of esterification of primary and secondary hydroxyls in cellulose. Mahoney and Purves (23), working with commercial ethyl cellulose

combined data from tosylation and iodination with lead tetraacetate and periodate oxidation and were able to conclude that the first-order rate constants for tosylation of the unsubstituted hydroxyls for the second, third and sixth position are in the ratios of 2.3, 0.07 and 15 respectively. Similar work has been done on partially hydrolysed cellulose acetate by Purves and Gardner (35) to give the ratios of 2.16, 0.106 and 23.4 for the hydroxyls at the number two, three and six positions.

Honeyman (36) investigated extensively the mechanism of tosylation and concluded that for heterogeneous substitution, esterification occurred much faster at number six hydroxyl of the glucose unit. There seemed to be little or no steric effect hindering the reactions of the two secondary alcoholic groups with tosyl chloride although their degree of substitution would be much less than that at the primary position.

To determine the fraction of free primary hydroxyls present in a sample of partially hydrolysed commercial cellulose acetate, the same process of tosylation and iodination was used by Malm, Tanghe and Laind (37). This method depends on (a) complete tosylation of free primary hydroxyl groups, partial or complete tosylation of secondary hydroxyl groups, (b) subsequent replacement of *all* primary tosyl groups by iodine and *no* reaction of secondary tosyl groups. However, the results showed that when the tosylation and iodination time was extended, more than 1.00 iodine per glucose unit was noted. Three possible

explanations for the increase were investigated;
(1) the participation of secondary hydroxyl groups,
(2) an increase in weight-percent iodine which would result from the loss of tosyl groups without entrance of iodine,
(3) adsorbed iodine which would likewise contribute to high iodine content of the product. The last error should be eliminated when the iodinated samples are thoroughly extracted with dilute sodium thiosulphate.

Their investigation reported a slight loss of tosyl groups which occurred upon extended iodination. However, even when this is corrected in the calculations, the iodine introduced is still more than one per glucose unit. This clearly indicates the slow participation of secondary tosyl groups during iodination. With such a defect, this method does not fulfil the conditions required for the exact determination of primary hydroxyl groups. It is possible, however, by maintaining identical reaction conditions throughout, to detect differences in reactivities from samples of varied past histories.

More recently Heuser and co-workers (38) reported on the tosylation of cellulose regenerated from the xanthate and concluded from iodination results that the rate constant for substitution on the primary hydroxyl was 5.8 times that for the secondary position. From their calculations, a slight loss of tosyl groups was also observed which showed a discrepancy in the total degree of substitution from that of the sum of primary and secondary hydroxyls being tosylated.

In this work an attempt is made to employ the process of tosylation and iodination as outlined above, to study the changes in reactivities in the primary and secondary hydroxyl groups brought about by alternate wetting and drying cycles. Samples of cellulose were tosylated first and the total degree of substitution determined by the sulfur content. They were then subjected to iodination followed by iodine and sulfur analyses which gave the fractions of primary and secondary hydroxyl groups substituted.

The sulfur analyses are carried out by Parr Bomb fusion (39) with sodium peroxide and subsequent precipitation of the sulphate with barium chloride solution.

The iodine content in the iodinated tosyl cellulose samples is determined by Clark's method (40). The iodine in the cellulose is first converted into iodine bromide and then oxidized to iodic acid by heating the samples with bromine. The excess of bromine is converted into hydrobromic acid by adding formic acid. Finally, after the addition of potassium iodide, the iodine liberated is titrated against standard sodium thiosulphate solution to a starch end point. The reactions are shown below:

$$\underset{\text{in cellulose}}{-CH_2-I} + Br_2 \longrightarrow -CH_2Br + BrI$$

$$BrI + 2Br_2 + 3H_2O \longrightarrow HIO_3 + 5\,HBr$$

$$HIO_3 + 5KI + 5H^+ \longrightarrow 3I_2 + 3H_2O + 5K^+$$

$$2Na_2S_2O_3 + I_2 \longrightarrow S_4O_6^{=} + 2I^- + 4Na^+$$

In this method, six equivalents of iodine are liberated

from each iodide, therefore the determination can be made with great accuracy even when the amount of iodide originally present in the samples is very small.

EXPERIMENTAL

1. PREPARATION OF CELLULOSE SAMPLES

A quantity of high grade cotton linters, donated by the Hercules Powder Co., was dewaxed in four batches (I, II, III and T) of 120 gm. each by extraction for 48 hours in a 1500 ml. Soxhlet apparatus, with a mixture of ethanol and benzene (1:2 by volume). The linters were then dried in air and subsequently stored in a closed container until needed.

A. Swelling of Cellulose Samples with Distilled Water at 25± 0.1°C.

The samples of cellulose were swollen using a modification of the procedure outlined by Brickman(2). One hundred grams of air-dried, dewaxed cellulose was immersed in 3000 ml. distilled water at 25± 0.1°C., and allowed to soak for three hours without stirring. The sample was then filtered through a large Büchner funnel (with filter paper present to retain the fine fibres) under mild suction, and lightly pressed to remove excess water. A preliminary drying in air was followed by a more intensive drying in a desiccator over phosphoric anhydride, under vacuum. Fresh phosphoric anhydride was added at intervals and the desiccator again evacuated until no liquification was observed at the surface of the drying agent during twelve hours drying period. The sample was then considered dry. A portion of this was retained and the process of wetting and drying was repeated on the remaining dried linters in order to obtain a series of

dried samples having received up to fifteen wetting and drying cycles. All samples from the same series were stored in one desiccator over fresh phosphoric anhydride.

TABLE 1a*

Wetting Cycles of Cotton Linters in Distilled Water

Batch No. 1
Wetting temperature: 25 ± 0.1°C
Initial amount of cellulose swollen: 100 grams
in 3000 ml. distilled water

Sample No.	Wetting Cycle	Time Immersed (hours)	Period of drying in air (days)	Period of drying over P_2O_5 in vacuum (days)	Wt. of sample retained (grams)
I-0	0	0	0	0	10
I-1	1	3	3	4	10
	2	3	3	3	
I-3	3	3	2	3	6
	4	3	2	2	
I-5	5	3	2	3	6
	6	3	1	2	
I-7	7	3	2	4	6
	8	3	3	1	
I-9	9	3	2	3	6
	10	3	2	2	
I-11	11	3	1	4	6
	12	3	2	2	
I-13	13	3	2	2	6
	14	3	2	3	
I-15	15	3	2	2	6

Samples dried over phosphoric anhydride under vacuum and stored at room temperature in Desiccator No. A over phosphoric anhydride.

* This table and those following are assembled in order to keep a complete experimental record. Though the data under the columns 'time immersed' and 'drying in air' are fairly consistent, they are nevertheless listed in detail for reference.

TABLE 1b

Wetting Cycles of Cotton Linters in Distilled Water

Batch No. II
Wetting temperature: 25± 0.1°C.
Initial amount of cellulose swollen: 100 grams
in 3000 ml. distilled water

Sample No.	Wetting Cycle	Time Immersed (hours)	Period of drying in air (days)	Period of drying over P_2O_5 in vacuum (days)	Wt. of sample retained (grams)
II-0	0	0	0	0	10
II-1	1	3	3	2	10
	2	3	5	2	
II-3	3	3	2	2	6
	4	3	2	2	
II-5	5	3	2	2	6
	6	3	2	2	
II-7	7	3	1	2	6
	8	3	3	1	
II-9	9	3	2	3	6
	10	3	2	3	
II-11	11	3	2	3	6
	12	3	1	3	
II-13	13	3	2	2	6
	14	3	2	2	
II-15	15	3	2	2	6

Samples dried over phosphoric anhydride under vacuum and stored at room temperature in Desiccator No. B over phosphoric anhydride.

TABLE 1c

Wetting Cycles of Cotton Linters in Distilled Water

Batch No. T
Wetting temperature: 25 ± 0.1°C
Initial amount of cellulose swollen: 20 grams
in 600 ml. distilled water

Sample No.	Wetting Cycle	Time Immersed (hours)	Period of drying in air (days)	Period of drying over P_2O_5 in vacuum (days)	Wt. of sample retained (grams)
T-25-0	0	0	0	0	10
T-25-1	1	3	1	1	2
	2	3	2	1	
T-25-3	3	3	1	3	3
	4	3	1	3	
T-25-5	5	3	1	3	2
	6	3	1	1	
T-25-7	7	3	1	1	3
	8	3	1	2	
T-25-9	9	3	1	1	3
	10	3	1	1	
T-25-11	11	3	1	1	3
	12	3	1	2	
T-25-13	13	3	1	2	3
	14	3	1	1	
T-25-15	15	3	2	1	3

Samples dried over phosphoric anhydride under vacuum stored at room temperature in Desiccator No. C over phosphoric anhydride.

B. Swelling of Cellulose Samples with Distilled Water at 50 ± 5°C

Twenty grams of cotton linters were immersed in 600 ml. distilled water at an elevated temperature of 50 ± 5°C. This was brought about by heating the beaker containing the linters in a water bath (with paraffin floating at the surface of the bath to minimize cooling by evaporation) which was in turn heated on a regulated hot plate. Filtration and drying procedures were identical to the previous experiments. The process was repeated on the dried linters up to 5 cycles.

TABLE 2

Wetting Cycles of Cotton Linters in Distilled Water at Elevated Temperature.

Batch No. T
Wetting Temperature: 50 ± 5°C.
Initial amount of cellulose swollen: 20 grams in 600 ml. distilled water

Sample No.	Wetting Cycle	Time Immersed (hours)	Period of drying in air (days)	Period of drying over P_2O_5 in vacuum (days)	Wt. of Sample retained (grams)
T-50-1	1	3	1	1	3
	2	3	1	1	
T-50-3	3	3	1	3	3
	4	3	1	1	
T-50-5	5	3	1	1	3

Samples stored as usual in Desiccator No. C.

C. Swelling of Cellulose Samples with Distilled Water at 75 ± 5°C

Twenty grams of dewaxed cotton linters were treated with water according to procedure B above but at 75 ± 5°C. The process was repeated on the dried linters to the extent of 5 cycles.

TABLE 3

Wetting Cycles of Cotton Linters in Distilled Water at Elevated Temperature

Batch No. T
Wetting temperature: 75 ± 5°C
Initial amount of cellulose swollen: 20 grams
in 600 ml. distilled water

Sample No.	Wetting Cycle	Time Immersed (hours)	Period of drying in air (days)	Period of drying over P_2O_5 in vacuum (days)	Wt of sample retained (grams)
T-75-1	1	3	1	3	3
	2	3	1	2	0
T-75-3	3	3	1	4	3
	4	3	1	1	0
T-75-5	5	3	1	1	3

Samples stored as usual in Desiccator No. C.

D. Swelling of Cellulose Samples in Ice-Distilled Water Mixture

The linters were immersed without stirring in 600 ml. ice-distilled water mixture. The small amount (less than 10 gm.) of ice floating at the surface was present to keep the temperature at 0°C. The entire beaker was then, in turn, surrounded by a bath of water-ice mixture. After three hours the floating ice was

decanted, the water removed by filtration and the linters dried as before. This process was again repeated on the dried linters, minus a sample, up to 15 cycles. (see Table 4).

E. Swelling of Cellulose Samples with Steam.

The dewaxed linters were loosely packed in the middle of a stoppered glass column (2 cm. in diameter). The small glass tubes through the stoppers at both ends served as steam inlet and outlet. After three hours of soaking with steam from a steam generator, the sample was gently pressed to remove excess water and then dried as before. This was repeated for 15 cycles.

TABLE 4

Wetting Cycles of Cotton Linters with Ice-Distilled Water Mixture.

Batch No. T
Wetting temperature: 0°C.
Initial amount of cellulose swollen: 30 grams
in 600 ml. ice-water mixture.

Sample No.	Wetting Cycle	Time Immersed (hours)	Period of drying in air (days)	Period of drying over P_2O_5 in vacuum (days)	Wt. of sample retained (grams)
T-0-1	1	3	1	4	3
	2	3	1	1	
T-0-3	3	3	1	3	3
	4	3	1	2	
T-0-5	5	3	1	3	3
	6	3	1	1	
T-0-7	7	3	1	1	3
	8	3	1	1	
T-0-9	9	3	1	2	3
	10	3	1	1	
T-0-11	11	3	1	1	3
	12	3	1	2	
T-0-13	13	3	1	2	3
	14	3	1	1	
T-0-15	15	3	2	1	3

Samples were stored as usual in Desiccator No. D.

TABLE 5

Wetting Cycles of Cotton Linters with Steam

Batch No. T
Wetting temperature: Around 100°C.
Initial amount of Cellulose soaked: 30 grams

Sample No.	Wetting Cycle	Time soaked in steam (hours)	Period of drying in air (days)	Period of drying over P_2O_5 under vacuum (days)	Wt. of sample retained (grams)
T-S-0	0	0	0	0	10
T-S-1	1	3	1	1	3
	2	3	1	3	
T-S-3	3	3	1	2	2
	4	3	3	1	
T-S-5	5	3	2	2	3
	6	3	1	3	
T-S-7	7	3	1	3	2
	8	3	1	1	
T-S-9	9	3	1	1	3
	10	3	1	2	
T-S-11	11	3	1	1	3
	12	3	1	1	
T-S-13	13	3	1	2	3
	14	3	1	2	
T-S-15	15	3	1	1	3

Samples were stored as usual in Desiccator No. D.

F. Preparation of Chemically Reactive Cellulose

The adopted procedure was developed by Purves and co-workers (14) and modified by Glegg (41). Ten grams of dewaxed, air-dried cellulose (from Batch No. III) were immersed in 360 ml. of 10% sodium hydroxide solution at 5°C. Three hours later, a calculated amount of 10% aqueous acetic acid (also previously cooled to 5°C) was poured into the mixture to neutralize the bulk. After the mixture was stirred for 10 minutes, the aqueous portion was decanted through a filter funnel and the linters lightly pressed to remove excess liquid. A second treatment with one litre of 1% acetic acid for 10 minutes rendered the solution slightly acidic and removed the last trace of sodium hydroxide. This solution was decanted as before and replaced by one litre of distilled water. The mixture was again thoroughly stirred and the liquid drained away. The washings with distilled water were repeated until the linters were free of acid (litmus test).

The wet mass was then gently squeezed from excess water and quickly dispersed in one litre of reagent methanol. This washing was repeated three more times followed by two more immersions of 30 minutes each, in 100 ml. magnesium dried methanol (42). One litre of thiophene free, sodium-dried benzene was then employed to replace methanol. Two more such washings of 15 minutes each completed this solvent exchange process.

The swollen linters now wet with benzene, were dried as usual over phosphoric anhydride under vacuum until the sample became free from the odour of benzene. It was then stored in Desiccator No. E over concentrated sulfuric acid.

G. Swelling of Cellulose Samples at Different Temperatures.

One more series of samples was prepared being wetted only once. The wetting temperatures are recorded in the second column of the following table. The procedure was stricly identical to that employed in A. to E. as previously outlined (pages 21 to 30).

TABLE 6

Cotton Linters Wetted Once at Different Temperatures

Batch No. III
Wetting interval: 3 hours.
Initial amount of cellulose swollen: 5 grams in 150 ml. distilled water.

Sample No.	Wetting Temperature	Period of drying in air (days)	Period of drying over P_2O_5 under vacuum (days)	Wt. of sample retained (grams)
III -no wetting	-	-	-	5
III-0	0°C	1	3	5
III-25	25 ± 5°C	1	3	5
III-50	50 ± 5°C	1	3	5
III-75	75 ± 5°C	1	3	5
# III-S	100°C	1	3	5

# III-S was soaked in steam without immersion in water as before. Samples were stored as usual in Desiccator No. D.

2. NITRATIONS WITH SULFURIC ACID -NITRIC ACID MIXTURES

The nitration procedure employed by Brown (43) was adopted here but with slight modifications. A technical nitration mixture was prepared according to Dorée (23) to yield cellulose nitrate of about 11 percent nitrogen. The nitrating mixture was checked by sample nitrations of dewaxed, unswollen cellulose. To ensure duplicable results, the nitrating procedures were carefully controlled and faithfully replicated throughout the different sample series.

The technical nitration solution (150 gm.) was weighed into a dry, 250 ml. Erlenmeyer flask, which was then immersed in a thermostated bath with temperature kept at 17± 0.1°C. After the flask and its contents had been brought to the bath temperature, 1.5 gm. of the dried cellulose was quickly weighed out (to the second decimal place), roughly shredded with forceps, and submerged in the nitrating solution for 30 minutes. A mixmaster working at low speed was used for stirring to ensure uniform diffusion of the acid. The thirty-minute reaction time was chosen to conform with that employed in commercial manufacture, and the reaction temperature of 17°C was such as to reduce degradation and side reactions (23), yet still allow maxiumum nitration to take place within half an hour.

The acid was removed by filtration with suction through a coarse, sintered-glass funnel; the residual nitrocellulose was gently pressed to remove excess fluid,

and then thrown, piece by piece into 400 ml. of rapidly stirred cold (about -15°C) ethanol-water mixture (1:1 by weight) (44). The liquid was again filtered from the solid by suction, through the same funnel but into a second suction flask. (The addition of ethanol to nitrating solution might cause an explosion). Two more such washings with 150 ml. each of cold ethanol-water mixture were followed by four similar immersions in the same aqueous ethanol at room temperature to ensure the complete removal of the free acids (litmus test).

The washed cellulose nitrate was subsequently stabilized by boiling three times, each time of five minutes duration, in 150 ml. quantities of a 1:1 ethanol-water mixture. Such treatment is reported to remove any bound sulphuric acid thus to yield a thoroughly stable product (44, 45). The hot solution was filtered as before and the ester then transferred into a weighing bottle to be dried over phosphoric anhydride under vacuum; the drying agent being changed at intervals until no further liquification of the anhydride occurred. The samples were stored over phosphorous pentoxide in a desiccator for subsequent analysis.

The technical cellulose nitrates thus obtained were colorless and fibrous, but the texture had a more brittle character than was shown by the original untreated cellulose, suggesting the occurrence of degradation during nitration.

3. DETERMINATION OF NITROGEN CONTENT

A. Correction for Moisture Absorption

Since the nitrated cellulose stored in the bone-dry state over phosphoric anhydride is extremely hygroscopic, erroneous values in their weights occurred due to moisture absorption during manipulation of these samples. To eliminate this error, samples were placed in tared weighing bottles and thoroughly dried over phosphoric anhydride, then rapidly capped and weighed in their bone-dry state. The weighing bottles were then uncapped and exposed to room conditions for two days and re-weighed. From the increase in weight the percentage of moisture absorbed was calculated and the true weight of the samples could be obtained by the following equation:

$$\frac{100 - \%\ \text{moisture absorbed}}{100} \times \text{sample weight} = \text{true sample weight}$$

Nitrogen contents were then calculated on the basis of this true sample weight.

B. Analyses of Nitrogen by Semi-micro Nitrometer

Rapid, accurate analyses were carried out on cellulose nitrate samples using a hand-shaken model of the Du Pont Semi-micro Nitrometer built to the specifications of Elving and McElroy (24)

The compensator tube (Fig. 4), nitro-cellulose burette as well as the connecting capillary from Stopcock 1 to 2 were calibrated by mercury displacement to convert scale readings in centimeters to volumes in millilitres. This data was plotted and all readings from the scales were

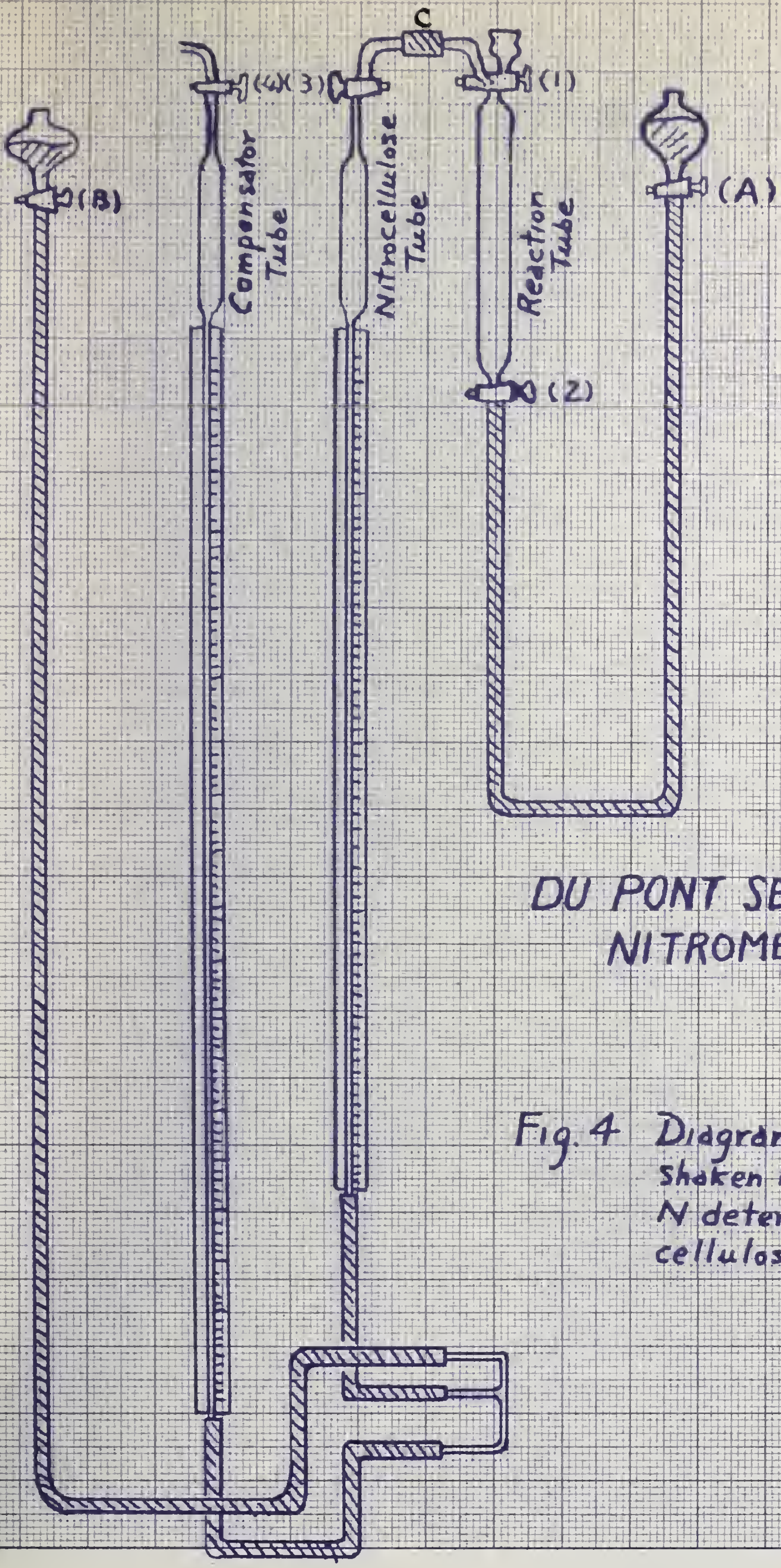
converted to volumes by use of the graph.

Initially the compensator tube, nitro-cellulose burette, reaction tube, and all connections and capillaries were completely filled with purified mercury (46), care being taken to remove any air bubbles present. With the system thus filled, Stopcocks 1, 3 and 4 were closed and the levelling bulbs A and B adjusted approximately to the height of these stopcocks.

The apparatus was standardized with potassium nitrate (24). About 105 mg. of potassium nitrate (recrystallized twice from water, washed with alcohol and dried in an oven at 150°C) was accurately weighed to the fourth decimal place. Since at standard temperature and pressure, 100 mg. of pure potassium nitrate give 22.15 ml. of nitric oxide, to calculate the theoretical volume at the same conditions, the following equation was used:

$$\text{Theoretical volume} = \frac{\text{Wt. } KNO_3\text{(mg.)}}{100} \times 22.15$$

The weighed potassium nitrate was transferred into the cup on top of the reaction tube and the tared glass weighing cup was re-weighed. The sample was washed into the reaction tube with six 1-ml. portions of concentrated, nitrogen-free, sulfuric acid, using a 1 ml. pipet with rubber bulb attached. It is extremely important that no air be admitted with the sample. Stopcock 1 was closed and the reaction tube disconnected from the nitrocellulose burette and shaken until gas pressure forced down the mercury to approximately an inch from the bottom Stopcock 2.



DU PONT SEMI-MICRO
NITROMETER

Fig. 4 Diagram of the hand shaken model used in N determination of cellulose nitrates

This Stopcock, 2, was then closed and shaking continued for a number of times each of about two minutes duration. Reaction was deemed complete only when there was no sign of further increase of gas pressure after Stopcock 2 was re-opened during the short intervals between shakings. Care was taken to keep the mercury in the capillary above Stopcock 1 by keeping a finger protected from acid by paper over the end during the shaking process. The reaction tube was then connected to the nitrocellulose burette by the rubber coupling C, in such a manner, that the ground-glass faces fitted firmly together.

The capillary above Stopcock 4 was filled with mercury, then 4 was opened and sulfuric acid-dried air from a spare reaction tube was drawn in, by lowering the levelling bulb B, to give a volume slightly greater than that calculated for the sample used. Bulb B was then gradually raised through a screw levelling device to give the correct volume by expulsion of excess air and Stopcock 4 was immediately closed. The correct volume reading was made when the mercury in Bulb B is at the same height as the mercury in the compensator tube.

Bulb B was then raised slightly above the level of the top of the apparatus; Stopcocks 1 and 3 were opened in that order so that mercury would flow to the reaction tube and thus rinsed the sulfuric acid from the capillary below Stopcock 1. After a few seconds, 1 and 3 were closed in that order and Bulb B was lowered to about the middle of the apparatus. The levelling bulb A was then raised

gradually, at the same time, Stopcocks 2, 1, 3, were opened in that order, and the gas transferred from the reaction tube to the nitrocellulose burette until the acid in the reaction tube came just to the top edge of Stopcock 1, whereupon 3, 1, and 2 were closed. The levelling bulb B and compensator tube were then adjusted so that with the mercury in the nitrocellulose burette, and compensator tube at the same level, the reading on the nitrocellulose burette corresponded to the calculated theoretical volume. The scale reading on the compensator tube was then recorded and used as the standardization mark for subsequent determinations, since it now would convert all readings to standard conditions. To ensure good results, a check on standardization was run every other day throughout the analytical period.

To make an analysis, it was necessary to know the approximate nitrogen content of the sample, on the basis that 100 mg. of 14% nitrogen would give a volume of approximately 23 ml. A sample of approximately 130 mg. of the 10-11% N containing nitrates was found to be suitable here.

The sample was accurately weighed out and transferred into the cup on top of the reaction tube as in the standardization. It was then introduced into the reaction tube by flushing with six 1-ml. portions of concentrated sulfuric acid and judiciously pushing the sample particles through the bore of the stopcock with a smooth-ended fine tantalum wire. This was a very delicate manipulation since all the sample must be well rinsed into the reaction tube with a limited amount of acid, and at the same time no air

admitted. The reaction tube was disconnected and shaken as in the standardization, but the compensator tube was left untouched. The gas was transferred to the burette as before. To take a reading, the columns of mercury in the nitrocellulose burette and compensator tube were again adjusted so that they were on the same level and coincided with the standardization mark on the compensator tube, the reading on the nitrocellulose burette was then recorded. This was the volume of nitric oxide at standard conditions. The per cent nitrogen was calculated from the equation:

$$\text{Per cent nitrogen} = \frac{\text{vol. in ml. NO} \times 62.56}{\text{sample weight in mg.}}$$

The nitrocellulose burette was emptied by forcing the gas back into the reaction tube leaving the capillary between Stopcocks 1 and 3 full of mercury. The gas and acid were then forced out from the reaction tube by raising the levelling bulb A with both Stopcocks 1 and 2 open. The cup and reaction tube were rinsed with a small amount of sulfuric acid which was expelled as before and the unit was ready for the next determination. Total time required for one analysis was about one and one-half hours.

To convert % nitrogen into degree of substitution the following equation was applied:

$$\frac{\text{D} \times \text{At. wt. of Nitrogen}}{\begin{array}{l}\text{Submolar wt. of cellulose}\\ \text{Nitrates (i.e. per anhydroglucose}\\ \qquad\text{unit)}\end{array}} = \frac{\%\text{N}}{100}$$

D = Degree of Substitution

$$\frac{14\ \text{D}}{(162.2 + \text{D}(46-1))} = \frac{\%\text{N}}{100}$$

$$\text{D} = \frac{162.2}{\left(\frac{1400}{\%\text{N}} - 45\right)}$$

4. OXIDATION OF NITROCELLULOSES WITH LEAD TETRAACETATE

Purification of Ethyl Acetate

Pure, dry ethyl acetate was prepared according to Fieser (47). Commercial ethyl acetate (12 liters) was washed three times with an equal volume of 5% aqueous sodium carbonate to remove acetic acid. It was then washed with the same quantity of saturated calcium chloride solution to remove any ethanol present. The washed ethyl acetate was dried overnight with anhydrous sodium carbonate, then for 3 hours with phosphoric anhydride, from which it was then decanted and fractionally distilled once with an all-glass apparatus under anhydrous conditions.

Purification of Glacial Acetic Acid and Acetic Anhydride

Four liters of acetic acid were freed from aldehyde by heating for three hours under reflux with 10 gm. of chromic anhydride, added in small quantities at suitable intervals to avoid violent reactions. The acid was then fractionated in an all-glass apparatus.

Acetic anhydride was purified by fractionation.

Preparation of 0.1 N Lead Tetraacetate in Glacial Acetic Acid

A good grade of lead tetraacetate was made according to Dalton (48). A mixture of 900 ml. of purified glacial acetic acid and 200 ml. of acetic anhydride was heated to 50°C in a 2-liter, 3-necked, round-bottom flask, fitted with a thermometer and a mechanical stirrer. Red lead (250 gm.) previously dried at 150°C for 6 hours and

subsequently cooled in a desiccator, was added in 30 gm. portions, each successive addition being made only when the color of the oxide previously added had vanished (the color of the solution, at that time, was pale-pink). The temperature must be kept below 65°C throughout the reaction period. The solution was allowed to cool in the stoppered flask, and the lead tetraacetate crystallized out in long, colorless needles. The acetate was then separated from the liquid by filtration with gentle suction, and washed four times with small portions of cold purified glacial acetic acid.

A 0.1 N acetic acid solution of the lead tetraacetate was prepared immediately, since the colorless needles darken rapidly if exposed to water vapor in the air. This color might be removed by re-crystallization with charcoal from hot glacial acetic acid.

The strength of the solution thus prepared was determined by pipetting 20 ml. of the liquid into 30 ml. of a sodium acetate buffer (consisting of 20 gm. of potassium iodide plus 250 gm. of sodium acetate per liter of aqueous solution) and the liberated iodine was titrated with 0.02 N sodium thiosulphate (27) to a starch end point.

Oxidations of Cellulose Nitrate

About 0.5 gm. of the prepared nitrocellulose, corrected for moisture absorption, was weighed to four decimal places in a capped weighing bottle and transferred into a 200 ml. glass-stoppered volumetric flask. The sample was covered with 125 ml. of purified, anhydrous ethyl

acetate, and slowly dissolved by agitation on a mechanical shaker for two to three days. Fifty ml. of 0.1N lead tetraacetate in glacial acetic acid was added followed by enough ethyl acetate to bring the total volume to the 200 ml. mark. The flask was well shaken again and set into a constant temperature bath at 25 ± 0.1°C. Two blanks were prepared simultaneously.

Consumption of lead tetraacetate by the nitrate was determined by amperometric titrations with 0.02N sodium thiosulphate (49). The apparatus (Fig. 5) consisted of a platinum rotating electrode, operating at a rate of about 60 r.p.m., a saturated calomel half-cell to provide a steady voltage of 0.246V, and the two electrodes were connected to a micro-ammeter. The standard 0.02N sodium thiosulphate solution was added from an automatic micro-burette.

At suitable intervals the volumetric flasks were removed from the bath and shaken briskly. Suspended undissolved nitrocellulose, if any, was allowed to settle and then a 10 ml. aliquot was pipetted into 30 ml. of potassium iodide - sodium acetate solution (27) contained in a 300 ml. electrolysis flask. The pipet was flushed with 10 to 11 ml. of reagent ethyl acetate and the washings also added to the electrolysis flask. This is important since the viscosity of the solutions of cellulose nitrate in ethyl acetate varies with the nitrogen content of the nitrates. With this precaution, any error due to this variable could be eliminated. After the addition of 100 ml. of distilled

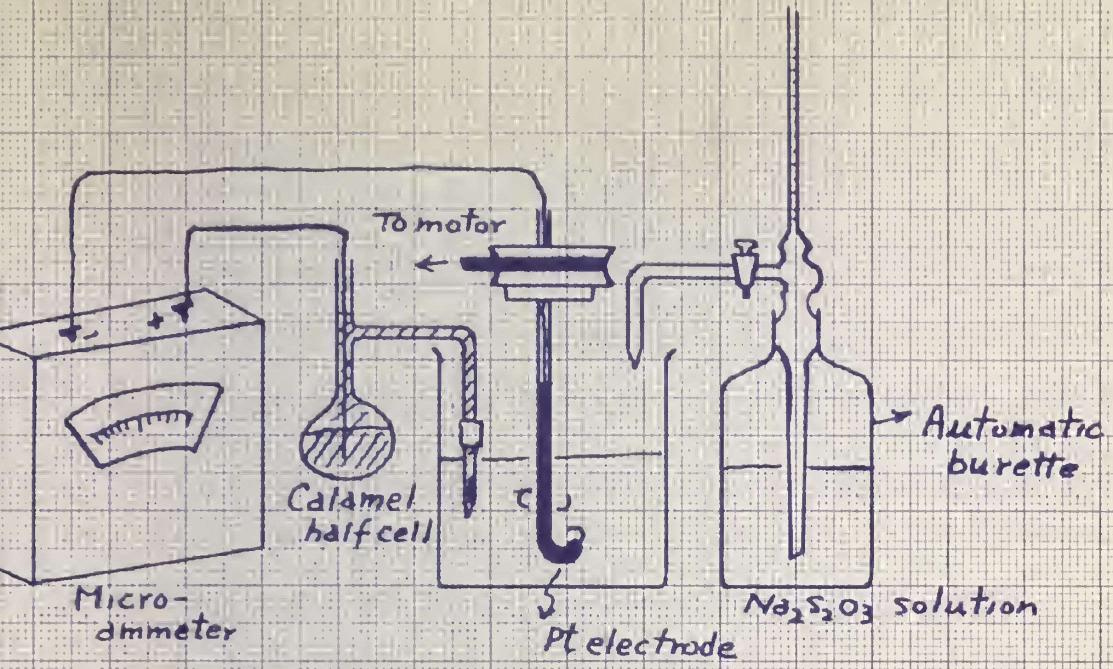


Fig. 5 Amperometric titration apparatus for $Pb(OAc)_4$ oxidation of nitrocellulose

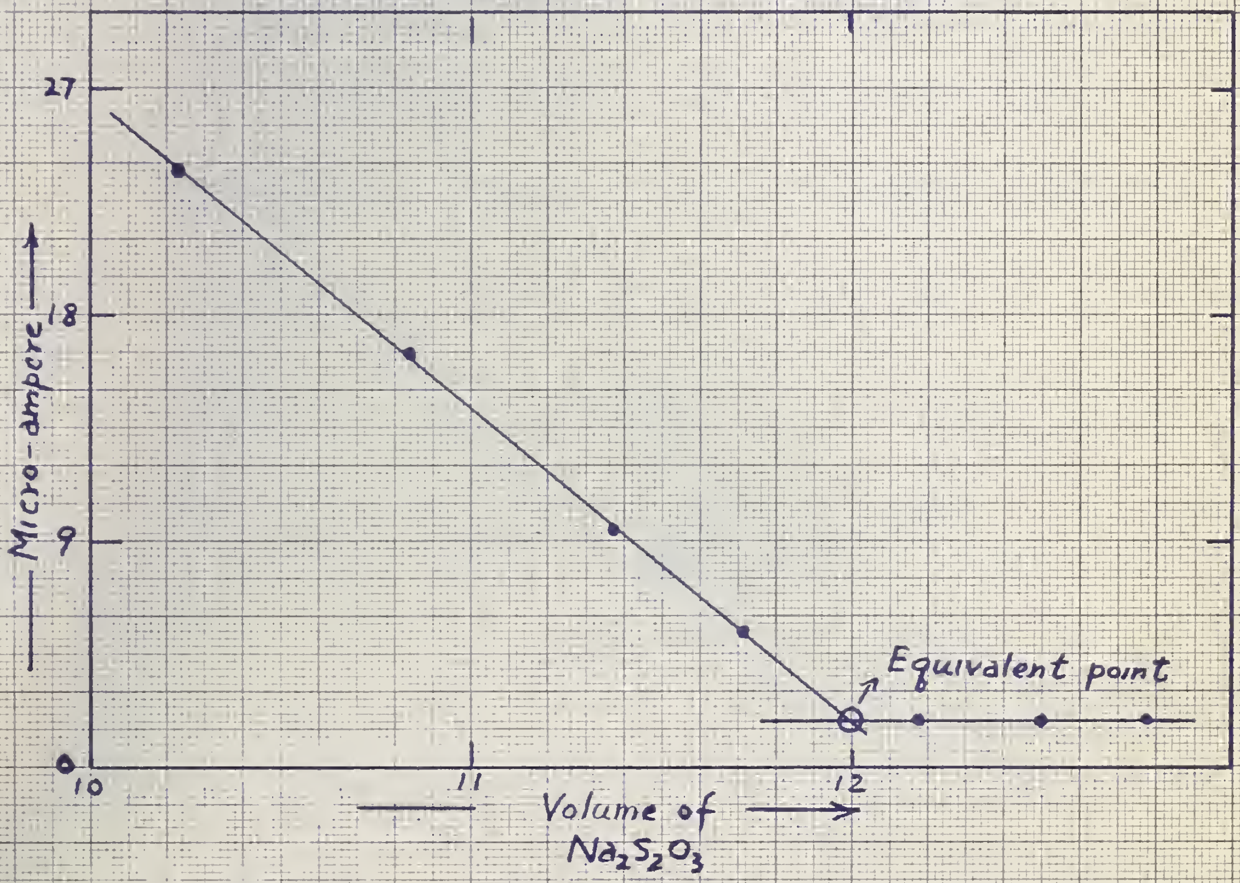


Fig. 6 Sample titration graph using amperometric method

water the contents of the flask was titrated with the two electrodes well immersed in the solution and the motor for the rotating platinum electrode in operation.

The course of titration was followed by the scale readings of the micro-ammeter. Usually 6 to 7 readings were recorded; 3 or 4 before and 3 after the equivalence point. This point was determined by plotting the volume of thiosulphate added against the corresponding micro-ampere reading on the scale (Fig. 6). Consumption of oxidant was expressed as the difference in titrations between the blanks and the sample.

An example of the calculation follows:

Corrected weight of cellulose nitrate = 0.5002 gm.

Volume of $Na_2S_2O_3$ used by 10 ml. aliquot from blanks (average) = 9.80 ml. (A)

Volume of $Na_2S_2O_3$ used by 10 ml. aliquot containing the sample after oxidation (average) = 8.98 ml. (B)

Consumption of $Na_2S_2O_3$ by 10 ml. aliquot of cellulose nitrate solution = (A) - (B) = 0.82 ml. (C)

Consumption of $Na_2S_2O_3$ by 200 ml. of cellulose nitrate solution = (C) × 20 = 16.40 ml.

Normality of $Na_2S_2O_3$ = 0.02787 N

Moles of oxidant consumed by sample = $\frac{0.02787 \times 16.40}{1000}$

Moles of oxidant consumed per glucose unit

$$= \frac{0.02787 \times 16.40}{1000} \times \frac{162}{0.5002} = 14.80 \times 10^{-2} \text{ moles}$$

Each sample of nitrocellulose was oxidized in duplicate for a period of approximately one thousand hours.

TABLE 9

Oxidations of Technical Nitrocelluloses with 0.1 N Lead Tetraacetate

T - No Wetting Sample (10.36 %N)

Oxidation Time (hours)	Consumption of Oxidant in Moles x 10^{-2} per Glucose Unit
72	6.63
120.1	12.70
168	-
216.1	18.61
288.3	22.65
336	25.77
384	28.34
480	33.09
552	36.62
631.5	41.91
720.2	46.25
840.4	53.71
1008.4	63.47

TABLE 10

Oxidations of Technical Nitrocelluloses with 0.1 N Lead Tetraacetate

T-0 series (wetted at 0°)

Oxidation Time	Consumption of Oxidant in Moles × 10^{-2} per Glucose Unit of samples			
(hours)	T-0-1 (10.20%N)	T-0-5 (10.46%N)	T-0-11 (10.59%N)	T-0-15 (10.61%N)
24.1	3.06	3.08	2.48	2.70
72	5.85	5.49	6.34	6.74
120	10.02	8.98	10.48	10.38
168	12.25	10.58	13.65	12.26
216	15.60	14.34	16.26	14.43
288.1	19.02	17.25	20.05	18.01
336	21.07	20.01	23.02	21.05
384	22.44	21.20	24.65	21.98
480	26.41	24.62	28.71	26.22
552	27.64	26.86	31.15	27.94
631.5	31.19	29.89	34.81	30.72
720.1	31.74	31.34	37.38	-
840.5	36.94	35.55	42.53	-
1008.5	50.49	40.68	52.69	-

TABLE 11

Oxidations of Technical Nitrocelluloses
with 0.1 N Lead Tetraacetate
T-25 series (wetted at 25°)

Oxidation Time	Consumption of Oxidant in Moles × 10^{-2} per Glucose Unit of samples			
(hours)	T-25-1 (10.29%N)	T-25-5 (10.39%N)	T-25-11 (10.51%N)	T-25-15 (10.52%N)
24	2.65	2.26	3.10	2.44
72	7.12	4.66	5.92	3.65
120	9.73	7.05	9.73	6.36
168	11.87	10.30	11.98	9.87
216	15.23	13.28	14.25	13.94
288	16.47	15.80	18.01	16.21
336	21.14	18.58	20.36	18.21
384	22.79	20.38	21.06	19.54
480	26.35	23.15	24.38	22.19
552	28.00	24.54	26.04	25.12
624	31.16	27.17	28.54	26.45
720.3	33.90	28.56	30.20	27.64
839.7	39.12	31.33	33.80	29.64
1009.2	-	35.35	41.69	33.09

TABLE 12

Oxidations of Technical Nitrocelluloses with 0.1 N Lead Tetraacetate

T-50 series (wetted at 50°)

Oxidation Time (hours)	Consumption of Oxidant in Moles × 10^{-2} per Glucose Unit of samples T-50-1 (10.41%N)	T-50-5 (10.22%N)
24	2.08	2.65
72	5.69	6.01
120	10.14	9.78
168	12.77	11.87
216	13.96	13.96
288	19.65	18.94
336	22.38	21.83
384	23.06	23.75
480	27.83	26.91
552	30.02	29.65
630	33.15	32.12
720	36.02	35.56
840	41.75	41.60
1008.1	49.53	46.82

TABLE 13

Oxidations of Technical Nitrocelluloses with 0.1 N Lead Tetraacetate

T-75 series (wetted at 75°)

Oxidation Time	Consumption of Oxidant in Moles × 10^{-2} per Glucose Unit of samples	
(hours)	T-75-1 (10.63%N)	T-75-5 (10.49%N)
24	4.21	2.26
72	5.19	6.07
120	7.85	9.32
168	9.96	12.00
216	13.21	14.13
288	15.85	16.79
336	18.47	20.67
384	19.43	21.78
480	23.02	24.83
552	24.12	26.08
624	26.46	28.86
720	28.26	31.36
839	30.60	35.62
1009	36.32	40.26

TABLE 14

Oxidations of Technical Nitrocelluloses with 0.1 N Lead Tetraacetate

T-S series (wetted in steam)

Oxidation Time	Consumption of Oxidant in Moles × 10^{-2} per Glucose Unit of samples			
(hours)	T-S-1 (10.30%N)	T-S-5 (10.24%N)	T-S-11 (10.19%N)	T-S-15 (10.16%N)
24	3.07	3.91	-	2.75
72	6.83	6.00	8.39	7.42
120	10.32	9.77	10.34	10.85
168	11.71	12.42	13.42	12.63
216	15.35	15.77	16.63	16.47
288	18.64	17.41	20.06	20.24
336	21.24	22.35	22.94	24.02
384	22.62	23.03	24.04	26.98
480	26.73	27.15	28.43	31.17
552	28.23	29.35	30.49	33.73
624	31.38	32.36	33.79	37.65
720	33.58	35.37	-	41.16
840	38.37	40.86	40.93	46.55
1008	45.09	45.41	48.07	55.05

5. ESTERIFICATIONS WITH p-TOLUENESULFONYL (TOSYL) CHLORIDE

A. Tosylations of Cotton Linters (38)

Reagents:

p-Toluenesulfonyl Chloride. Eastman Kodak Company (m.p. 65° - 68°), re-crystallized from di-ethyl ether. The re-crystallized material melted sharply at 67° - 68°.

Pyridine. Merck medicinal grade, dried over barium oxide and re-distilled just before use. B. pt. range 111° - 113°C.

Tosylation of Series I (ref. Table 30)

Samples (2.50 gm.) of the wetted and dried cellulose were weighed and placed in 250 ml. glass-stoppered flasks, Pyridine (50 ml.) was added to each flask, and the mixtures allowed to stand overnight in a thermostated bath at 25 ± 0.2°C. p-Toluenesulfonyl chloride (147.0 gm.) was dissolved in pyridine, brought to 25°, and made up to 250 ml. with pyridine. Into each flask (now at bath temperature) was pipetted 50 ml. of the pyridine - tosyl chloride solution (containing 29.4 gm. of tosyl chloride or 10 moles for each anhydroglucose unit of cellulose), and the pipet flushed with 30 ml. of pyridine. The flask was shaken to mix the contents thoroughly and then placed in 25° bath for a reaction time of 24.0 hours.

Composition of the reaction mixture:

Cellulose	2.5 gm.	(0.1623 moles per liter)
Tosyl chloride	29.4 gm.	(1.623 moles per liter)
Pyridine	130 ml.	

At the designated time the flask was removed from the bath and cooled in ice for two minutes, after which 100 ml. of ice-cold acetone containing 10 ml. of water was added slowly to decompose the remaining tosyl chloride. The mixture was allowed to stand in ice water for five minutes with occasional shaking and poured into 800 ml. of distilled water. The suspension was mechanically stirred for thirty minutes, after which it was filtered through a coarse sintered-glass funnel under mild suction and was washed well with about 1500 ml. of distilled water. The product was then suspended in 800 ml. of distilled water and allowed to stand overnight. The next day the sample was collected on a coarse sintered-glass funnel, washed well with distilled water, extracted with reagent methanol for 20 hours and then with diethyl ether for 24 hours in a Soxhlet apparatus, after which the sample was air dried at room temperature and, finally, in a vacuum desiccator over phosphoric anhydride.

Tosylation of series II (ref. Table 31)

The procedure was identical to that of Series I and prepared approximately three months later. The only step different was the omission of extraction with methanol after the tosyl cellulose samples were well washed (except Sample No. OA ref. Table 31, which was given

the methanol extraction). The reaction time was extended to 25.0 hours in the hope that more tosyl groups would be substituted.

Composition of the reaction mixture:

Cellulose	2.5 gm.	(0.1623 mole per liter)
Tosyl Chloride	29.4 gm.	(1.623 moles per liter)
Pyridine	130 ml.	

Tosylation of Series DI (ref. Table 34)

This series was prepared simultaneously with Series II and with identical procedures (i.e. without methanol extraction). The reaction time was extended to 29 hours.

Composition of the reaction mixture:

Cellulose	2.5 gm.	(0.1623 mole per liter)
Tosyl Chloride	23.5 gm.	(1.208 moles per liter, i.e. 3 moles for each anhydroglucose unit of cellulose)
Pyridine	130 ml.	

E. Iodination of Tosylated Cellulose (33)

Reagents:

Sodium Iodide: General Chemical Division reagent grade, dried at 120°C for two hours and cooled in desiccator just before use.

Acetonylacetone: Eastman Kodak Company product (b.p. 190 - 193°) was used as received.

All three tosylated series were iodinated by identical procedures. Dry sodium iodide (1.00 gm.)(weighed on the analytical balance) was dissolved in 100 ml. of

acetonylacetone in a 2-neck ground-glass round bottom flask and heated to 115 - 120° with a Glas-Col heating mantle through a rheostat. The flask was fitted with an air condenser and a thermometer. After the solution had reached the bath temperature, 1.00 gm. of the tosylated cellulose sample was added. The reaction was maintained for four hours and the flask vigorously shaken about once every hour.

At the designated time, the mixture was poured, with stirring, into 500 ml. of distilled water. This step was included because it was found that the more highly tosylated samples were partially dissolved in the reaction mixture during the iodination. The product was then collected on a coarse, sintered-glass filter and the sample was washed five times with 100 ml. portions of methanol. Then, 250 ml. of 0.1 N sodium thiosulphate was poured through;the material was removed from the filter, stirred twice with 250 ml. portions of 0.1 N sodium thiosulphate and, finally, washed on the filter again with a fourth portion of thiosulphate to remove any absorbed iodine. When thoroughly washed with distilled water, the product was extracted with ether in a Soxhlet apparatus for 24 hours. It was air dried and finally dried in a vacuum desiccator over phosphoric anhydride.

C. Sulfur Analyses - Parr Bomb Method

The tosylated samples were subjected to sodium

peroxide oxidation and the sulphate thus produced was precipitated as barium sulphate to be estimated gravimetrically (39). Approximately 0.2 gm. of the sample (weighed to four decimal places) was placed in a clean and dry fusion cup and 0.2 gm. of finely divided benzoic acid; 0.2 gm. of sucrose and 1.0 gm. of sodium perchlorate were added. (These weighings may be made on a simple torsion balance to the nearest tenth). This was followed by one level scoopful of sodium peroxide (about 15 gm.). The cup was then closed with the properly fitted cap and tightened with a wrench. The materials were mixed thoroughly by shaking the sealed cup and then the cup was tapped gently while in an upright position to loosen the chemicals from the sides and top of the container.

Water (3 ml.) was pipetted onto the top of the bomb which was then put inside a metal shield directly over the small opening. A hot, sharp flame was applied through this opening to the lower end of the bomb until the water began to boil (bubbles began to form). The flame was immediately removed and the reaction was allowed to continue for half a minute, then quenched by immersing the bomb in cold running water.

The bomb was opened carefully; the cup and cover then placed in a clean, 400 ml. beaker to which enough distilled water was added to come half way up the cup lying on its side. The beaker, covered with a watch glass,

was warmed gently to dissolve the fusion products. When complete solution of the material was ensured, the cup and cover were removed, first washing off the solution into the beaker. The stirred solution was neutralized with concentrated hydrochloric acid from a medicine dropper. A color change occurred at the neutral point (from pale grey to bright yellow). Two ml. acid was added in excess.

After all the carbon dioxide gas seemed to have escaped, the solution was filtered into a clean 600 ml. beaker to remove any insoluble impurities present, and then diluted to 400 ml. with distilled water. The liquid was heated just to boiling, whereupon 25 ml. of saturated aqueous picric acid followed by 10 ml. of 10% (by weight) barium chloride was added slowly from a burette while the solution was stirred. A white precipitate of barium sulphate formed. The hot solution was digested for at least twelve hours, whereupon it was filtered into a previously prepared and weighed Gooch crucible. The precipitate was washed well with about 200 ml. of hot water in small portions, then dried and weighed to constant weight.

Calculation.

1. $$\%\ \text{sulfur} = \frac{\text{At. wt. of S}}{\text{M.Wt. of BaSo}_4} \times \frac{\text{Wt. of BaSO}_4\text{ppt.}}{\text{Wt. of sample}} \times 100$$

e.g. Wt. of barium sulphate obtained = 0.0367 gm.
Wt. of tosylated sample used = 0.1967 gm.

$$\%S = \frac{32.05}{233.42} \times \frac{0.0367}{0.1967} \times 100$$

$$= 2.56\%$$

2. Conversion of % sulfur to no. of tosyl groups substituted per glucose unit.

Calculated from $\frac{100}{(162.14 + 154.18h_t)} = \frac{\%S}{32.05\ h_t}$

where h_t = tosyl groups per glucose unit

e.g. if %S = 2.56%

$$\frac{100}{(162.14 + 154.18h_t)} = \frac{2.56}{32.05h_t}$$

$$3205\ h_t = 2.56\ (162.14 + 154.18\ h_t)$$
$$(3205 - 394.5)h_t = 414.9$$
$$h_t = \underline{0.148}$$

i.e. 0.148 tosyl group substituted per glucose unit.

D. Iodine Analyses (40)

About 0.1 gm. of dry iodinated tosyl cellulose sample (weighed to four decimal places) was put into a clean and dry 300 ml. Erlenmeyer flask which contained 20 ml. of 10% potassium acetate in glacial acetic acid. The sample was oxidized by heating with 1 ml. of liquid bromine on a hot plate. It was found necessary to add a few glass beads to the flask to prevent bumping. Furthermore higher temperatures were avoided to prevent the bromine from escaping too rapidly. When the material was apparently all in solution, the beaker was cooled and the oxidized solution was diluted with 25 ml. of 25% sodium acetate solution and 100 ml. of distilled water. The excess of bromine was then reduced with 90% formic acid during a period of ten to fifteen minutes. The latter was added dropwise and the flask thoroughly swirled. Approximately one gram of potassium iodide and 10 ml. of 10% sulfuric acid were added, and

the liberated iodine was titrated with 0.02N sodium thiosulphate from an automatic micro-burette using a starch indicator for end point determination.

Calculation.

1. $$\% \text{ Iodine} = \frac{N \text{ of } Na_2S_2O_3}{1000} \times \text{vol. in ml. of } Na_2S_2O_3 \times \frac{\text{At. Wt. of I}}{\text{Wt. of sample}} \times 100$$

e.g. N of $Na_2S_2O_3$ = 0.01975 N
Vol. of $Na_2S_2O_3$ consumed = 7.25 ml.
Weight of sample used = 0.0987 gm.

$$\% \text{ I} = \frac{0.01975 \times 7.25 \times 126.39}{1000 \times 0.0987} \times 100$$

$$= 18.4\%$$

2. Conversion of %I and %S to number of primary hydroxyls substituted per glucose unit.

Calculated from $$\frac{100}{(162.14 + 154.18h_t + 109.92h_i)} = \frac{\%I}{126.92h_i}$$

where h_i = moles iodine per glucose unit

$$h_t = \frac{126.92h_i \ \%S}{32.05 \ \%I}$$

e.g. if S = 1.7%
I = 21.0%

$$154.18h_t = \frac{154.18 \times 126.92 \times 1.7}{32.05 \times 21.0} \times h_i$$

$$= 49.4 \ h_i$$

$$126.92 \quad 100 \ h_i = 21.0 \ (162.14 + 49.4h_i + 109.92h_i)$$

$$9346h_i = 3405$$

$$h_i = 0.364$$

i.e. 0.364 primary hydroxyl substituted per glucose unit.

3. Conversion of %I and %S to number of secondary hydroxyls substituted per glucose unit.

Calculated from

$$\frac{100}{(162.14 + 154.13h_t + 109.92h_i)} = \frac{\%S}{32.05h_t}$$

where h_t = moles tosyl per glucose unit

$$h_i = \frac{32.05h_t \quad \%I}{126.92 \quad \%S}$$

e.g. if $S = 1.7\%$

$I = 21.0\%$

$$109.92h_i = \frac{109.92 \times 21.0 \times 32.05h_t}{126.92 \times 1.7}$$

$$= 343h_t$$

$$3205h_t = 1.7\,(162.14 + 343h_t + 154.13h_t)$$

$$2360h_t = 275.6$$

$$h_t = 0.116$$

i.e. 0.116 secondary hydroxyl substituted per glucose unit.

RESULTS AND DISCUSSION

The entire experiment was carried out with cotton linters obtained from the same source and dewaxed under identical conditions but in four separate batches which are designated with prefixes I, II, III and T throughout this thesis.

Batches #I, #II and #T underwent alternate wetting-drying cyclic processes (See Experimental 1), the first two (I and II) being repeatedly wetted at 25° and dried, while the last one (T) was subdivided into five parts, each part being soaked and dried as above but at 0°, 25°, 50 ± 5°, 75 ± 5°, and in steam respectively. These series are identified by indexes T-0, T-25, T-50, T-75 and T-S. Part of #III was employed for the preparation of chemically reactive cellulose by the solvent exchange method (p.31), designated by the term III-R, and the remaining portion of III was again separated into five parts each being wetted only once at individually different temperatures as was #T. They are called III-0, III-25, III-50, III - 75 and III-S. All the samples thus prepared were stored over phosphorus anhydride with each wetting-drying series in its own individual desiccator.

In order to correlate the wetting temperatures with accessibilities of cellulose, technical nitration reactions were applied to the entire thirty samples of the T-series. Two samples of untreated dewaxed linters (zero wetting) were nitrated separately at the same time (the results of which might be used as a standard of comparison). Since

the equilibrium of the reaction i.e. the degree of nitration, depends essentially on the composition of the nitrating solution, one batch of HNO_3 - H_2SO_4- H_2O mixture was prepared and used throughout the entire experiment to eliminate any uncertainty in this respect.

The results from the nitrogen analyses are tabulated on page 63 and express the degree of nitration in terms of %N by weight. This is then converted to the corresponding number of hydroxyls nitrated per glucose unit by the appropriate equation (p. 40) and listed in Table 8 (p.64). The two zero-wetting nitrates give average values of 10.37% and 10.35%N respectively (p. 63) which are in surprisingly good agreement. This, in a way, serves as evidence for the consistency of the nitration procedures and the reliability of the nitrometer analyses.

Both T-0 and T-25 series show a continuous increase in nitrogen content as the wetting and drying cycles proceed onward (Table 7). The increase is greater in the case of wetting at 0°, i.e. from 10.20% to 10.63%N than that for 25° wetting (10.29% - 10.53%). These findings confirm the results reported by Brickman (2) and Rosenthal (1), who worked on a series of linters wetted at 25° only. When the N contents of T-0-1 and T-25-1 are compared with that of the zero wetting sample, a sharp decrease in accessibility is observed, again that of T-0-1 being more acute than T-25-1. This was also noted by Brickman (2) who offered the following explanation:

TABLE 7

NITROGEN ANALYSES ON NITROCELLULOSES*

(As Per Cent Nitrogen of Nitrated Linters)

Wetting Cycle	Wetting Series				
	T-0	T-25	T-50	T-75	T-S**
0	# 10.36	10.36	10.36	10.36	10.36
1	10.20	10.29	10.41	10.63	10.33
3	10.49	10.54	10.29	10.52	10.29
5	10.46	10.39	10.22	10.49	10.24
7	10.51	10.44			10.25
9	10.54	10.46			10.20
11	10.59	10.51			10.19
13	10.63	10.53			10.22
15	10.61	10.53			10.16

* Analysed by du Pont Semimicro Nitrometer

** T-0, T-25, T-50, T-75 and T-S were individually wetted at temperatures 0°, 25°, 50°, 75° and in steam respectively.

# Average of two samples with 10.35 and 10.37% N respectively

TABLE 8

NITROGEN ANALYSES ON NITROCELLULOSES*

(As Number of Hydroxyls Nitrated Per Glucose Unit)

Wetting Cycle	Wetting Series				
	T-0	T-25	T-50	T-75	T-S
0	1.799	1.799	1.799	1.799	1.799
1	1.758	1.781	1.812	1.871	1.793
3	1.834	1.847	1.781	1.842	1.781
5	1.826	1.807	1.763	1.834	1.768
7	1.839	1.820			1.771
9	1.847	1.826			1.758
11	1.860	1.839			1.756
13	1.871	1.844			1.763
15	1.865	1.844			1.748

---

* Converted from %N listed in Table 7 by equation on page 40.

The process of dewaxing with ethanol-benzene should involve some swelling by the polar solvent ethanol. As benzene and ethyl alcohol form an azeotropic mixture, with the proportions of solvents used, evaporation of the remaining mixture of solvent during air drying would remove the alcohol and leave some residual benzene to be finally eliminated. In effect this constitutes drying by solvent exchange (50, 51) resulting in at least a partial maintenance of the swollen state produced by the alcohol. The first wetting and drying cycle would therefore show a marked decrease in accessible cellulose.

In the case for series T-50 and T-75, the analyses show a trend opposite to that found for the T-0 and T-25 linters (Table 7). The sharp decrease in nitrogen content which occurs for the first wetting cycles in T-0 and T-25 as compared to the zero wetting samples has been replaced by an increase in reactivities. Furthermore, the accessibility decreases as the wetting cycles proceed. This latter phenomenon is not entirely unexpected since wetting and swelling of cellulose is an exothermic reaction (2); The increase of wetting temperature might hinder the swelling of the macromolecular chain and thus lead to a continuous decrease in the degree of substitution. The obvious increase in nitrogen contents for T-50-1 (10.41%) and T-75-1 (10.63%) as compared to that of zero wetting (10.36%) suggests a greater initial swelling of cellulose at higher temperatures reflected by their increase in

accessibility which is, however, overcome later by the repeated wetting and drying processes.

When cellulose was soaked in steam (series TS), the linters, in appearance, became more brittle and gathered into small lumps. Here again a gradual decrease in reactivity (10.30 to 10.16%N, Table 7) occurs with increase of wetting and drying cycles although the tendency is comparatively milder. The decrease in N content of T-S-1 from that of zero wetting, if significant, might be due to the general 'collapse' of the linters soaked in steam, rather than to the explanation cited for previous cases (p.62 , refer to T-0-1 and T-25-1). The same cause may be responsible for the decrease in accessibilities of the entire T-S series as a whole (refer to Fig. 7, p.67) as compared to the other four. The lumpy particles also give rise to more heterogeneity in nitration as noted during the nitrometer analyses, the results obtained from the same nitrocellulose samples being less consistent than the rest. Thus it seems undesirable to wet cotton linters in steam repeatedly because not only will the reactivities be reduced but also its heterogeneous nature will be greatly amplified.

Lead tetracetate oxidation was performed in duplicate on seventeen nitrocellulose samples (Table 15, p.69) whose nitrogen contents have been previously determined and range from 10.16% (T-S-15) to 10.63% (T-75-1) N by weight. Although the flasks were agitated on a mechanical shaker for three days most of the samples (0.5 gm. of

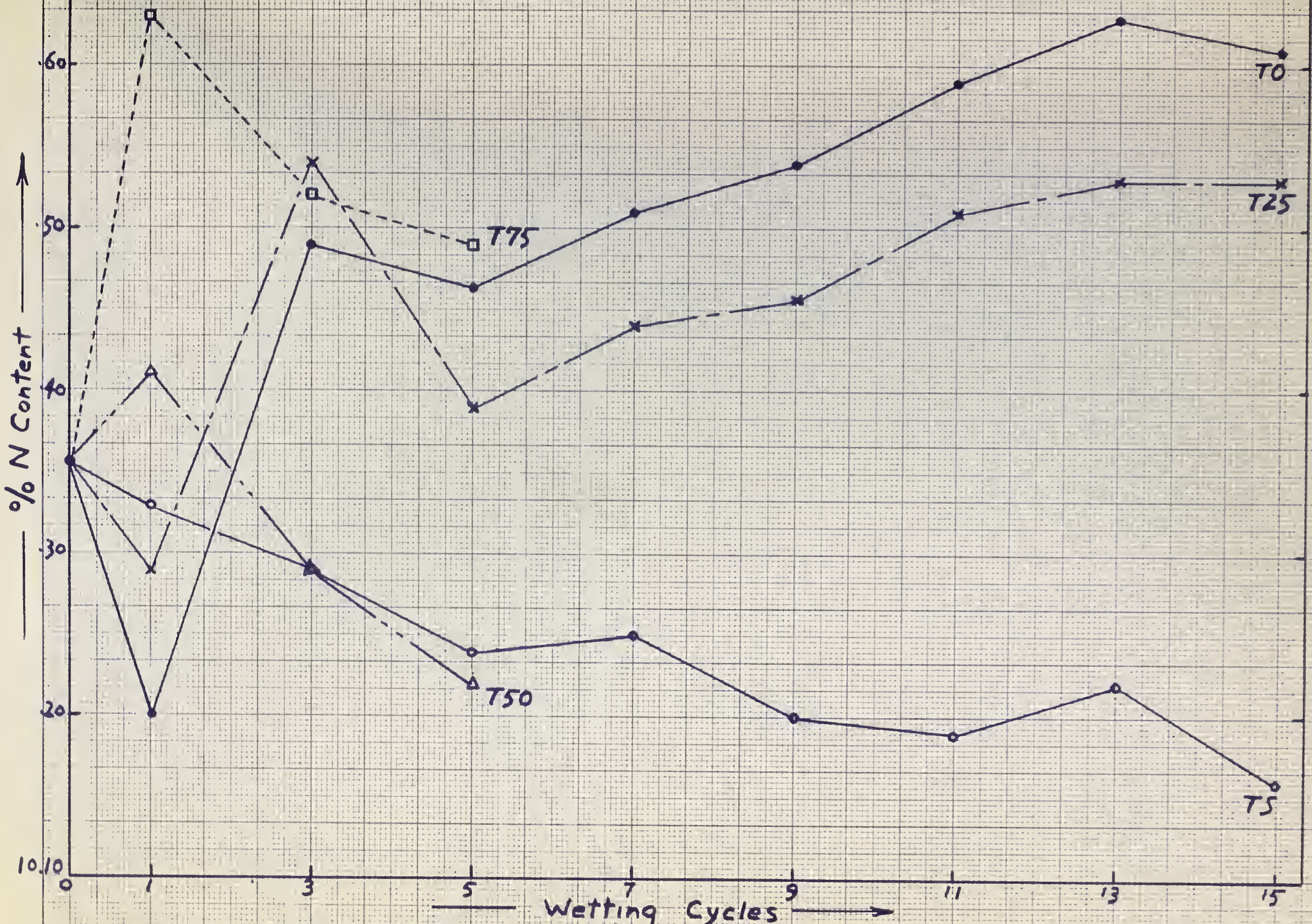


Fig. 7 % N by weight of the nitrocellulose samples series T

nitrocellulose in 125 ml. of ethyl acetate) still did not dissolve completely. They became transparent and gel- like. This was, however, considered suitable for oxidation since complete solution apparently is unnecessary for satisfactory reaction (23). Two blanks containing the oxidant in glacial acetic acid and ethyl acetate were prepared at the same time. All oxidations of the nitrocellulose samples were carried out with portions of the same lead tetraacetate stock solution in glacial acetic acid (normality 0.0969 N) to eliminate any differences which might occur in this respect.

It is found that amperometric titration gave much better end points than the usual starch technique. During test runs on Sample T-C-3 made to become familiar with the oxidation procedure a starch end point was used. It was found that when the bluish-violet coloration of starch disappeared, the thin organic layer of ethyl acetate still showed a very faint yellow color of iodine which usually required for its elimination about 0.1 ml. of 0.02N sodium thiosulfate solution. Therefore this was considered inaccurate and all further titrations were carried out amperometrically, which avoided the previous difficulties.

The consumption of lead tetraacetate by cellulose nitrate should reach a maximum when all the free glycols in the anhydroglucose units have reacted. However, in the present work, the consumption continued to rise in all the cases even after a period of twelve hundred hours. This phenomenon was first reported by Hockett and co-workers

TABLE 19

Consumption of Lead Tetraacetate by Cellulose Nitrates

	Sample Number	Moles Oxidant per Glucose Unit
(1)	zero wetting	6.7×10^{-2}
(2)	T-0-1	11.3×10^{-2}
	T-0-5	10.0×10^{-2}
	T-0-11	9.75×10^{-2}
	T-0-15	9.50×10^{-2}
(3)	T-25-1	9.0×10^{-2}
	T-25-5	10.4×10^{-2}
	T-25-11	11.1×10^{-2}
	T-25-15	11.7×10^{-2}
(4)	T-50-1	7.75×10^{-2}
	T-50-5	8.70×10^{-2}
(5)	T-75-1	10.5×10^{-2}
	T-75-5	10.7×10^{-2}
(6)	T-S-1	9.3×10^{-2}
	T-S-5	10.0×10^{-2}
	T-S-11	10.2×10^{-2}
	T-S-15	10.3×10^{-2}

(27) and was repeatedly observed by others (23,32,53). Nevertheless, this defect does not discourage the application of this method to our studies. When the consumption of the oxidant in moles per anhydroglucose unit was plotted against the period of oxidation in hours, a break in the oxidation curve could be observed which was taken to mark the end of the true glycol oxidation, and the subsequent much slower change was recorded as oxidation of the ethyl acetate (27) and/or other side reactions.

The titration data obtained seem satisfactory and the duplicates are generally in very good agreement. For simplicity, only one set of results is reported here. Tables listing the oxidation intervals against the consumption of lead tetraacetate for all the nitrocellulose samples are presented under the Experimental section. (pages 46 - 51) The corresponding curves (Fig. 8 - 13) plotted from the above two variables are shown on pages 71 to 79 . It is to be noted that all the breaks on the curves appear around the oxidation period of three hundred and fifty hours, indicating the termination of the glycol oxidation. In each case, the total consumption of the oxidant in moles per anhydroglucose unit is obtained from the intersection of the curve extrapolated to the ordinate. This is considered reasonable, since the amount of lead tetraacetate consumed by the glycol units is a definite one and should be equal to the difference between the consumption by the entire system minus the consumption due to other types of oxidation.

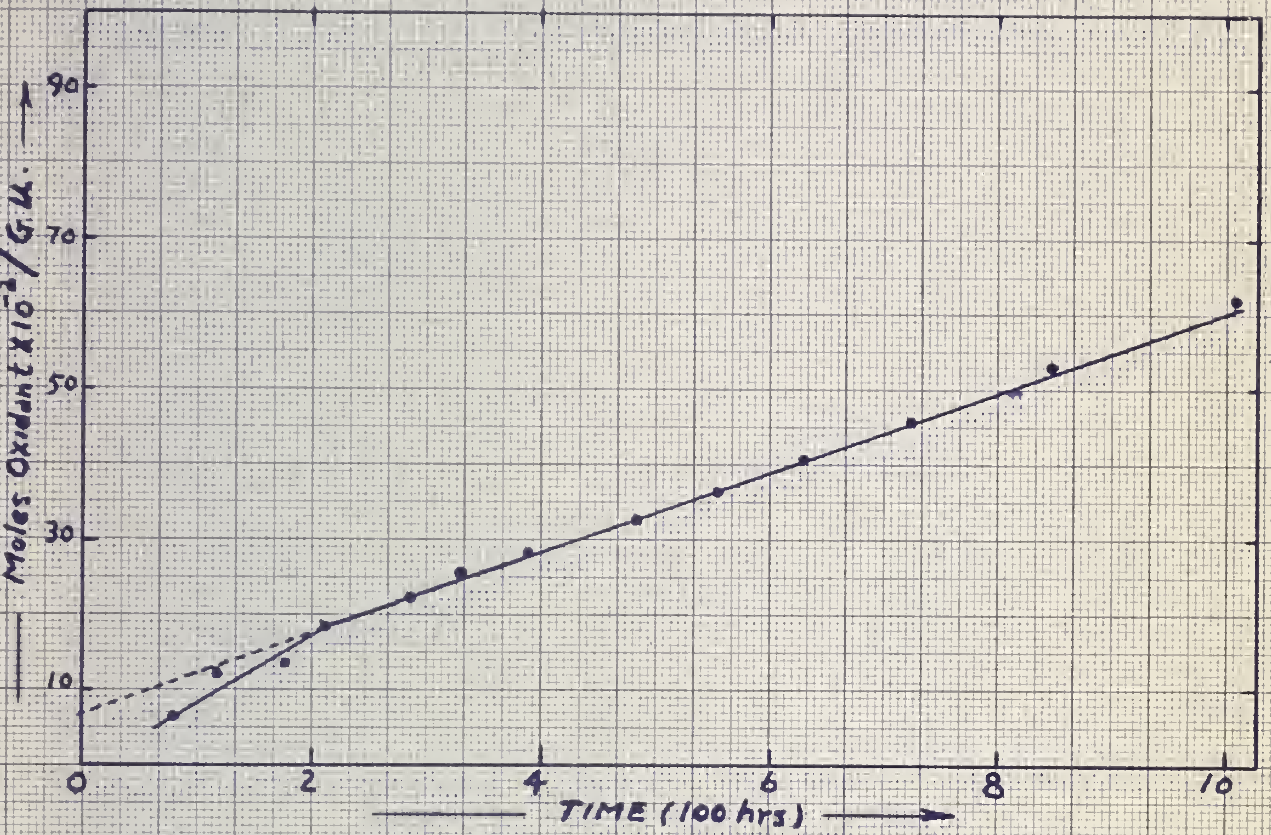


Fig. 8 $Pb(OAc)_4$ oxidation of cellulose nitrates
Zero Wetting Sample

HUGHES OWENS 315N·METRIC

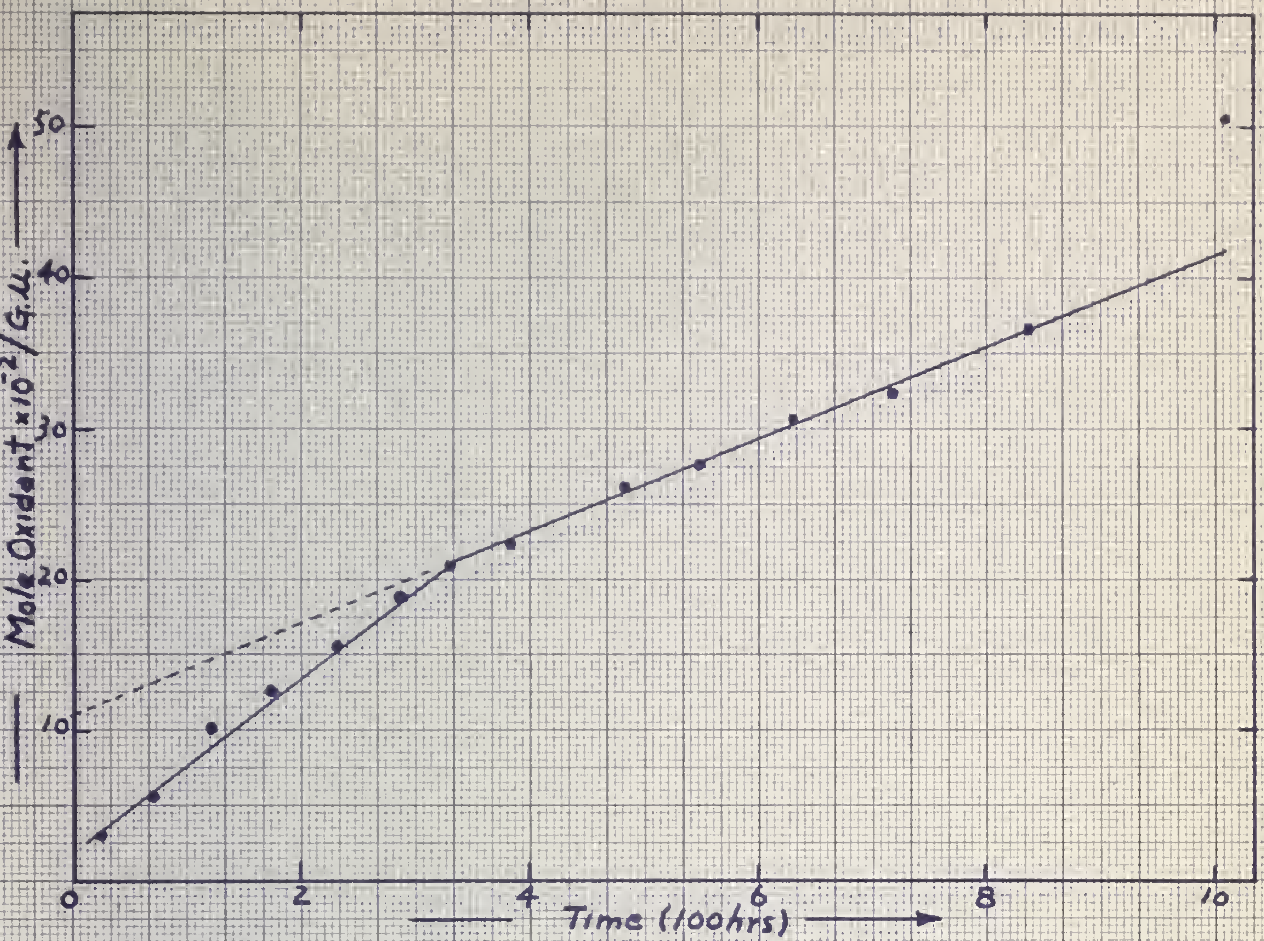


Fig. 9a Pb(OAc)$_4$ oxidation of sample T-0-1

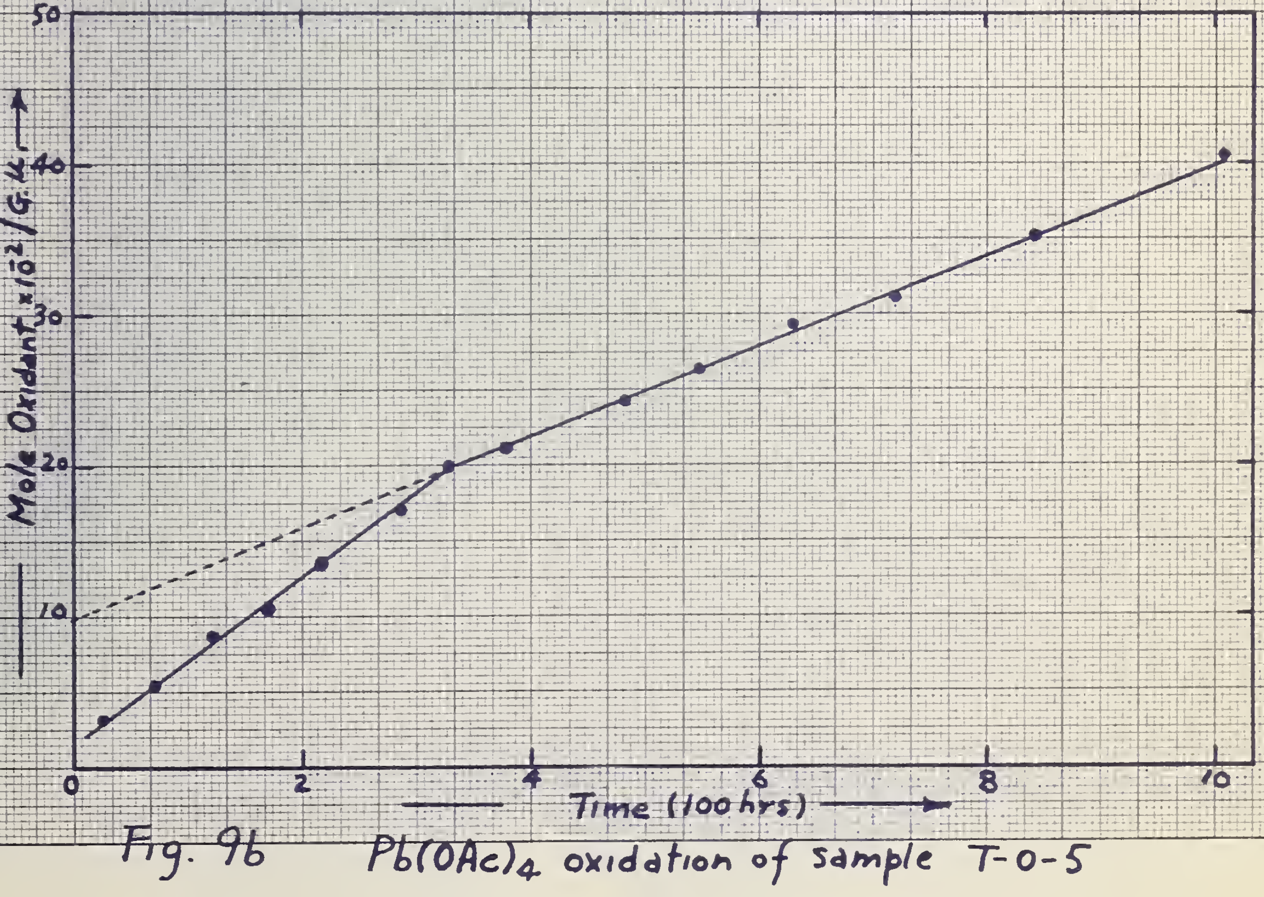


Fig. 9b Pb(OAc)$_4$ oxidation of sample T-0-5

(T3)

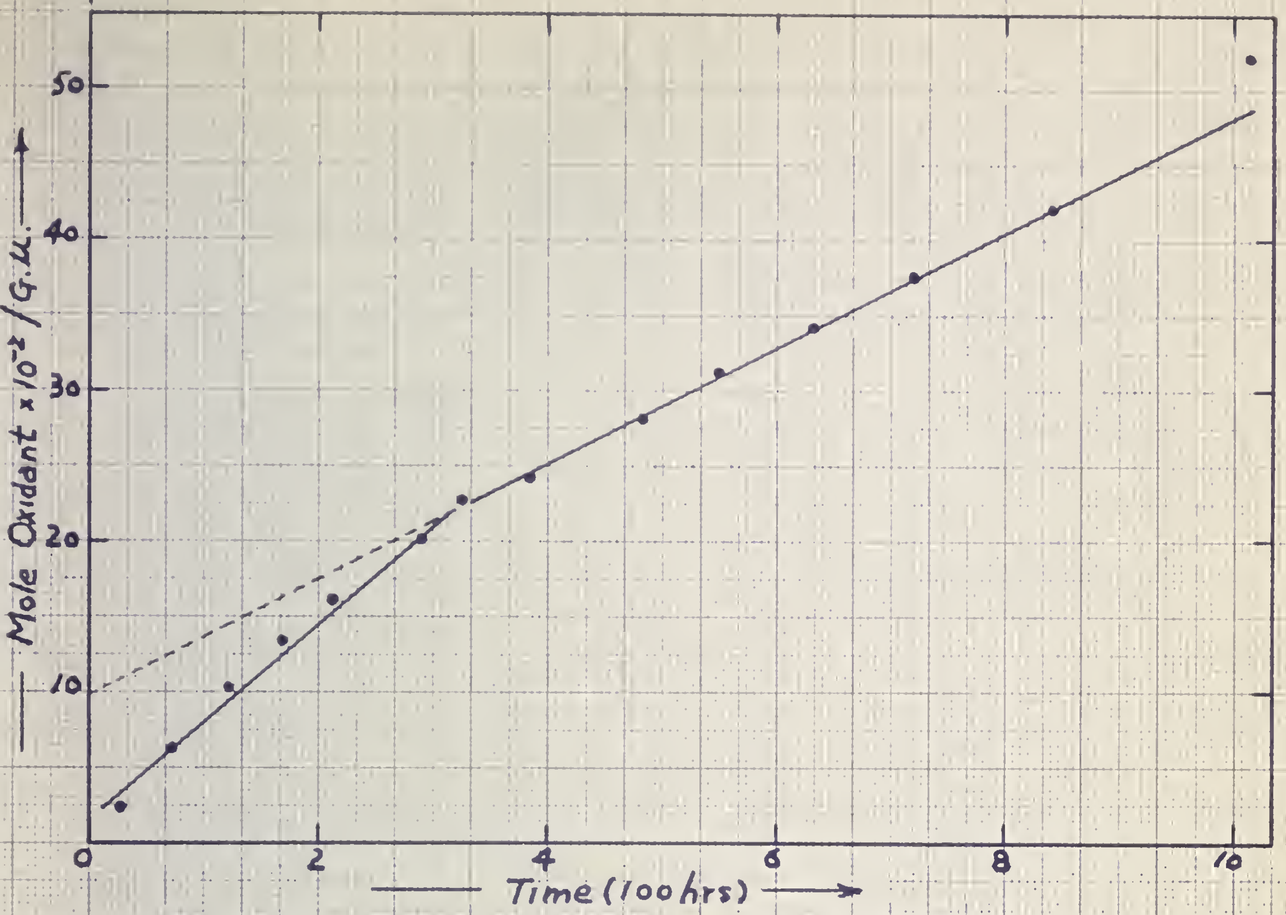


Fig. 9c $Pb(OAc)_4$ oxidation of sample T-0-11

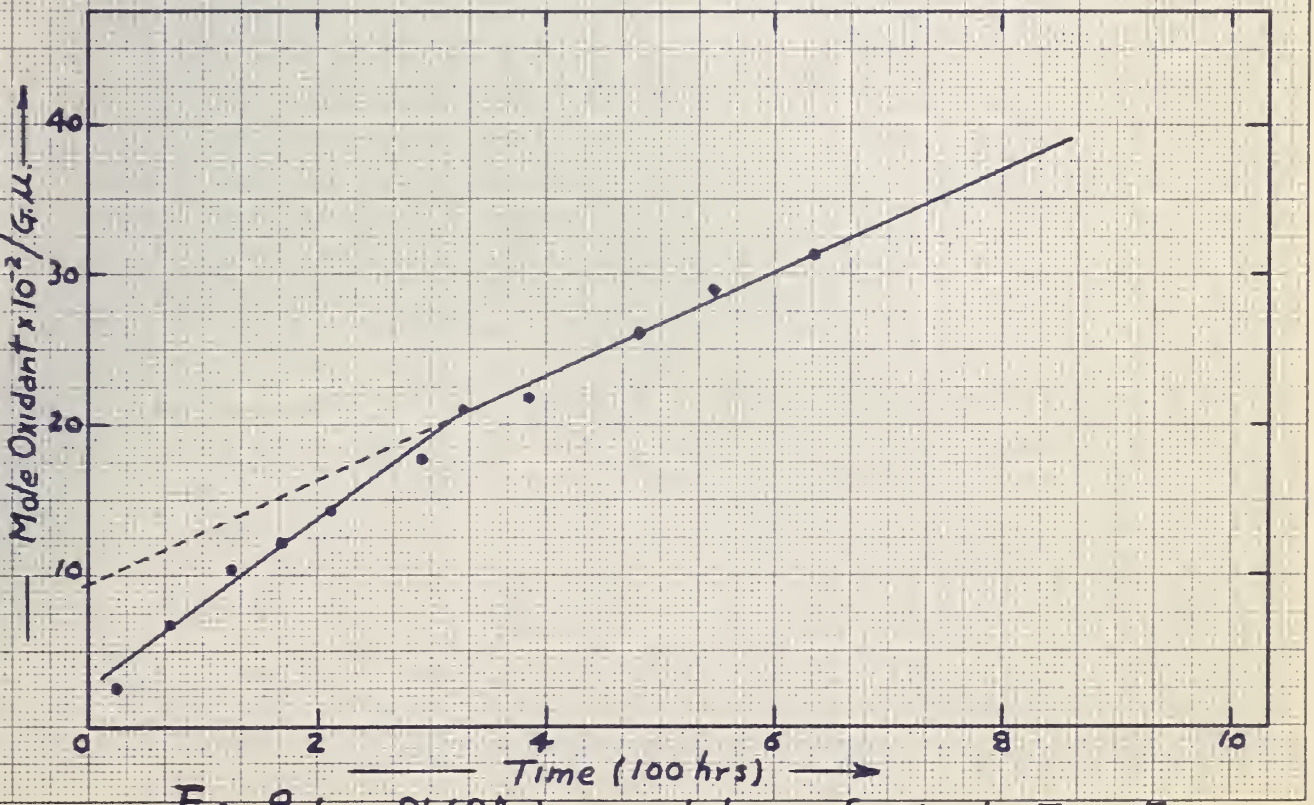


Fig. 9d $Pb(OAc)_4$ oxidation of sample T-0-15

HUGHES OWENS 315 M-METRIC

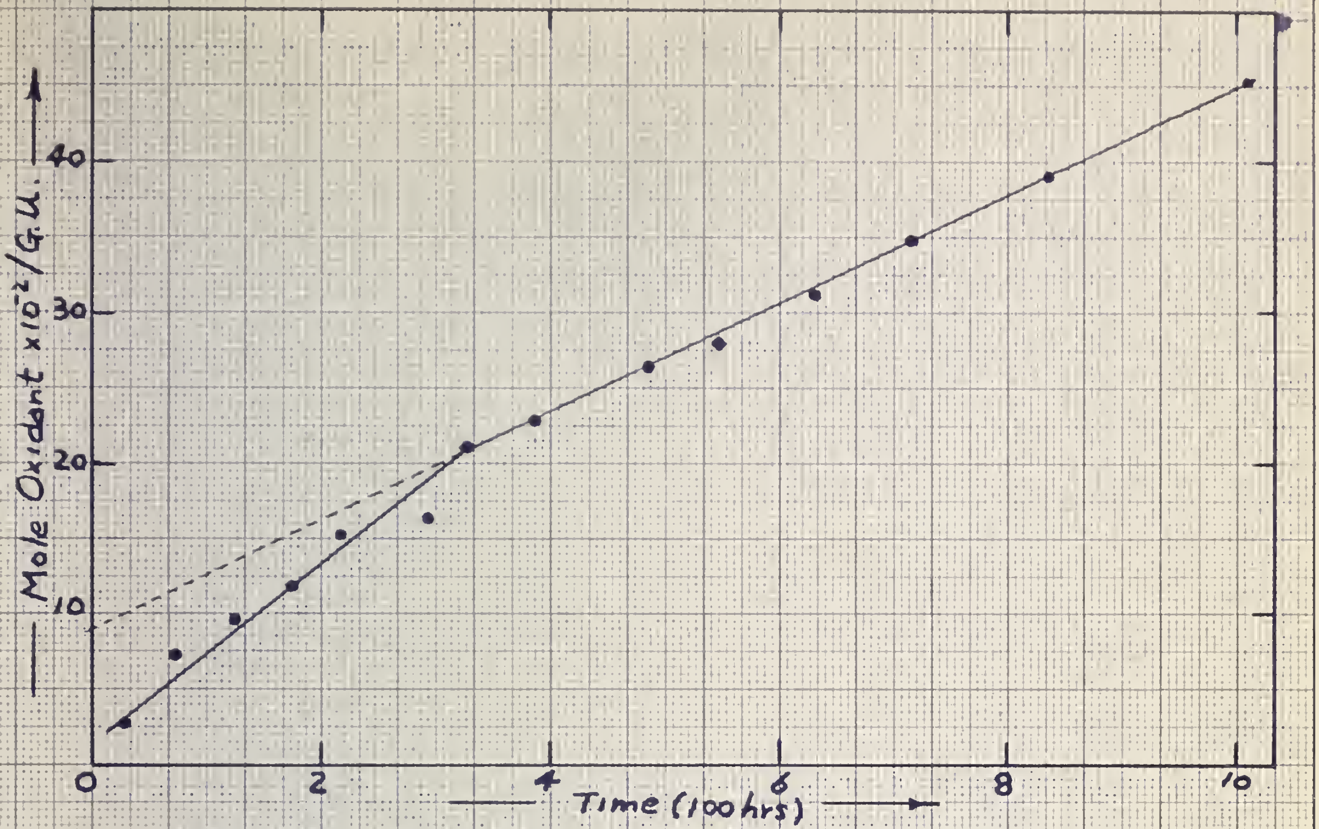


Fig. 10a Pb(OAc)$_4$ oxidation of sample T-25-1

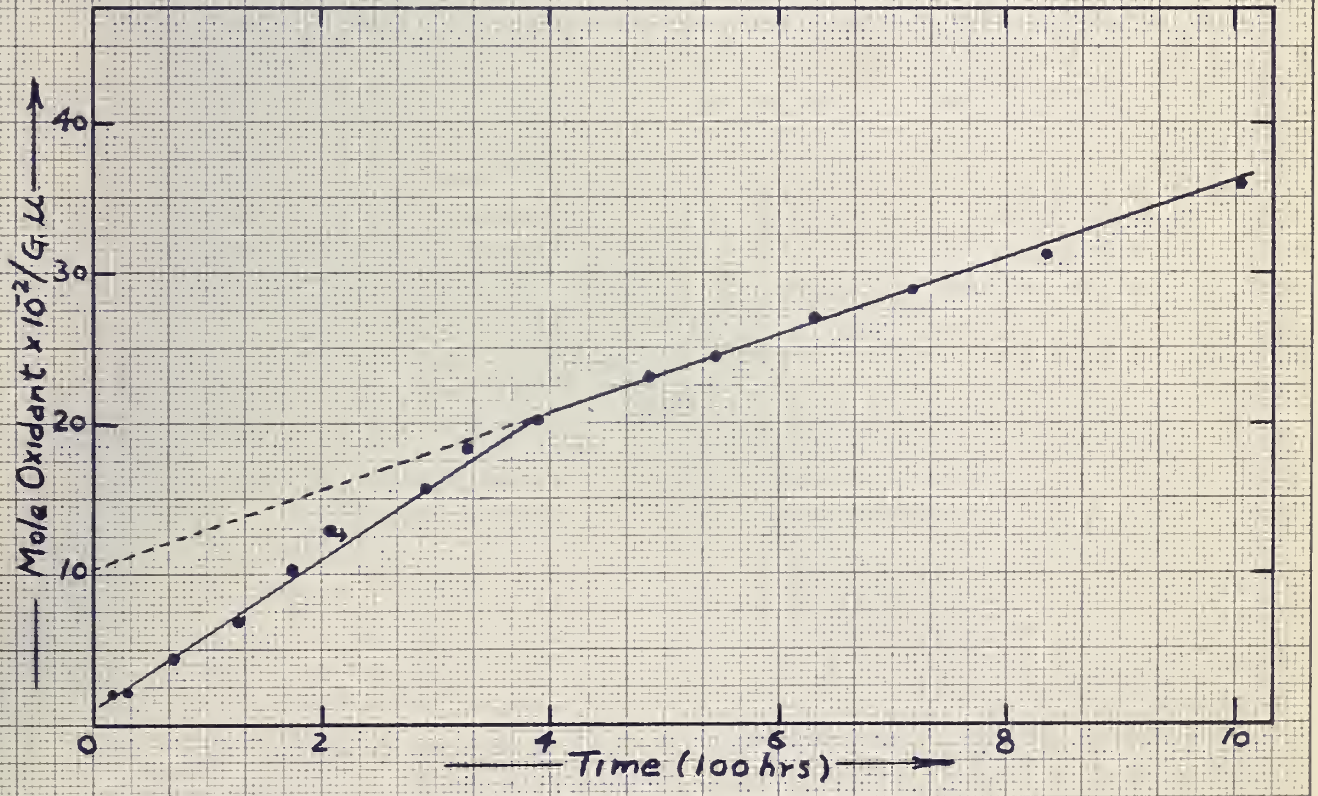


Fig. 10b of T-25-5

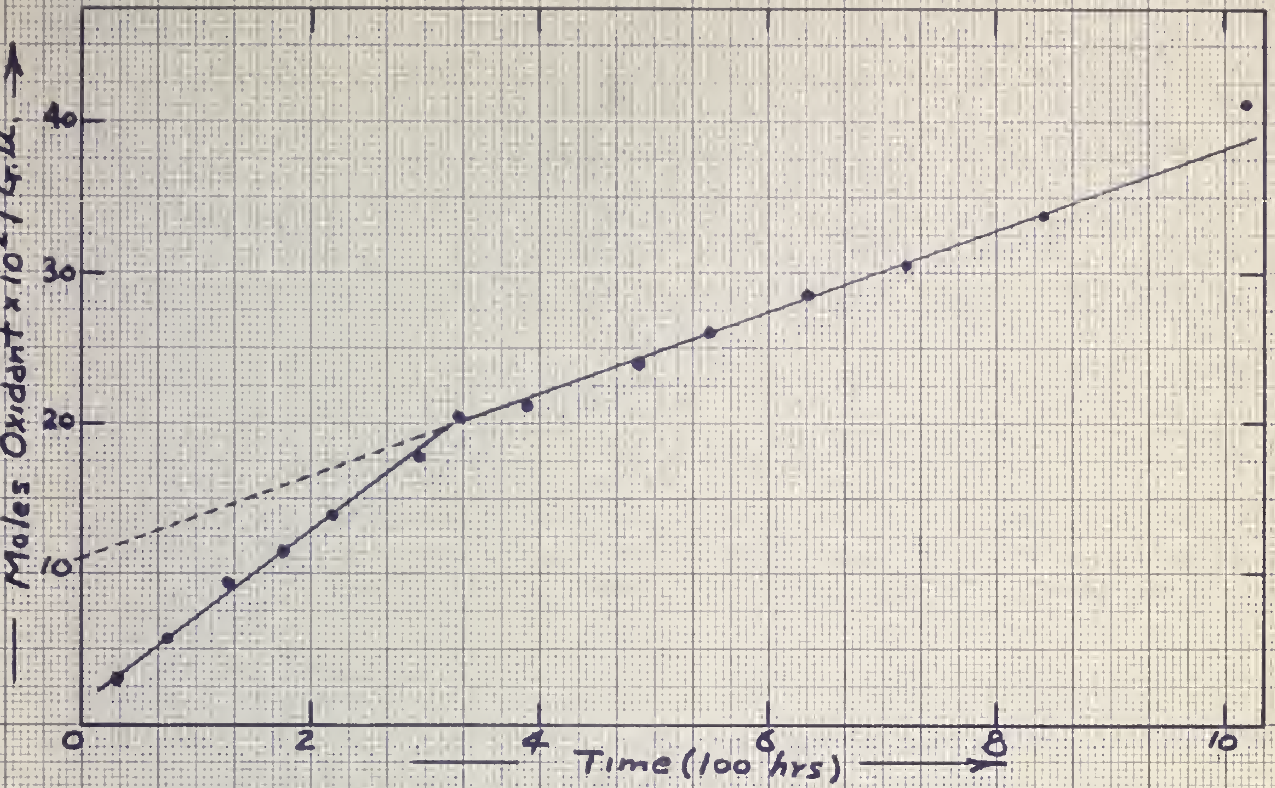


Fig. 10c of T-25-11

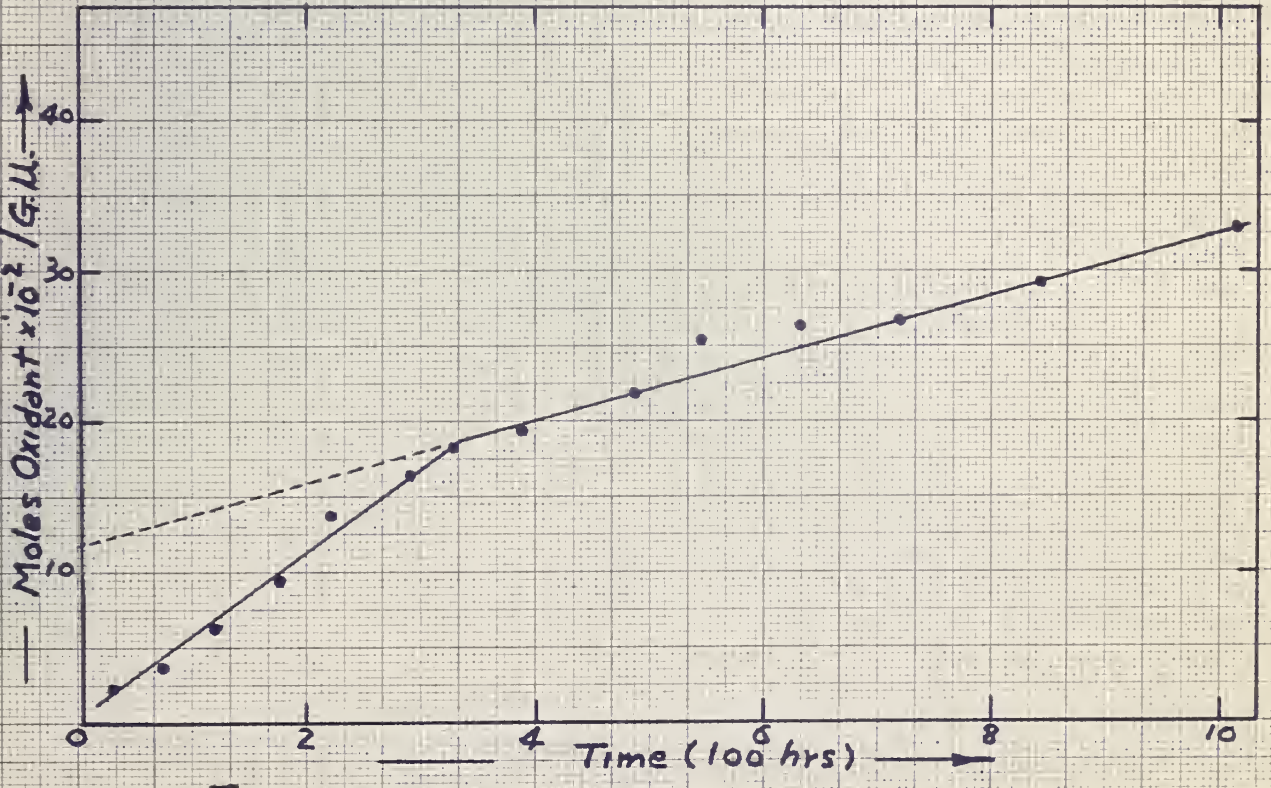


Fig. 10d of T-25-15

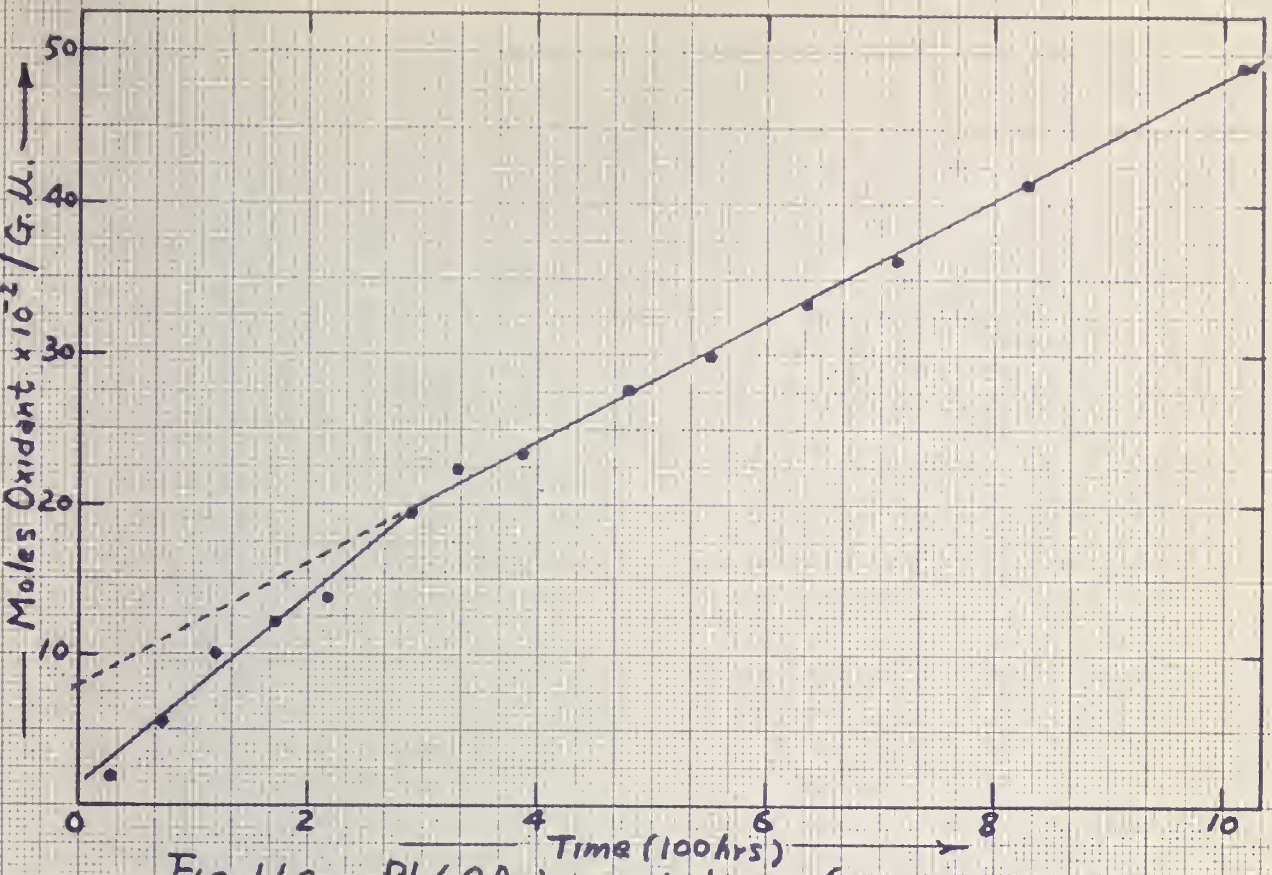


Fig. 11a $Pb(OAc)_4$ oxidation of sample T-50-1

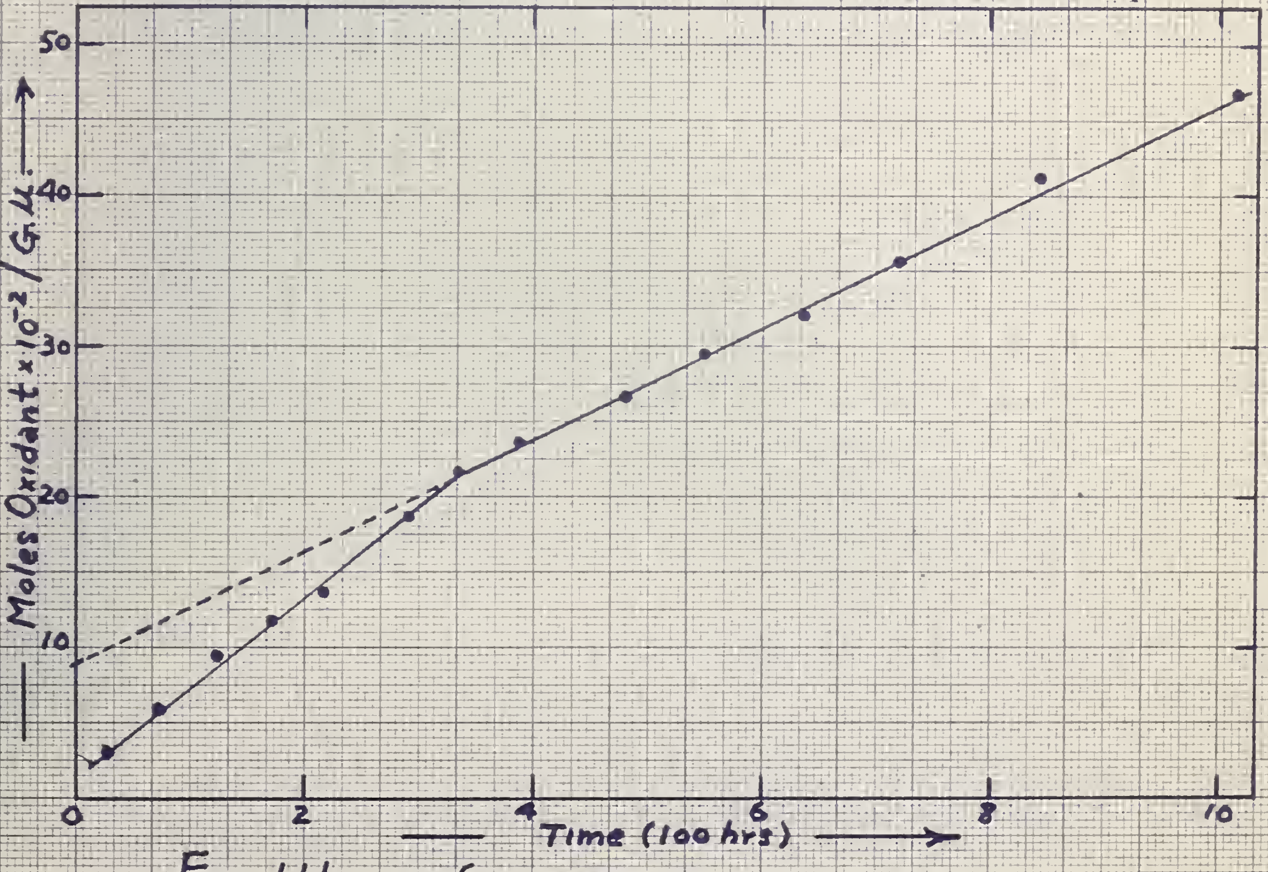


Fig. 11b of T-50-5

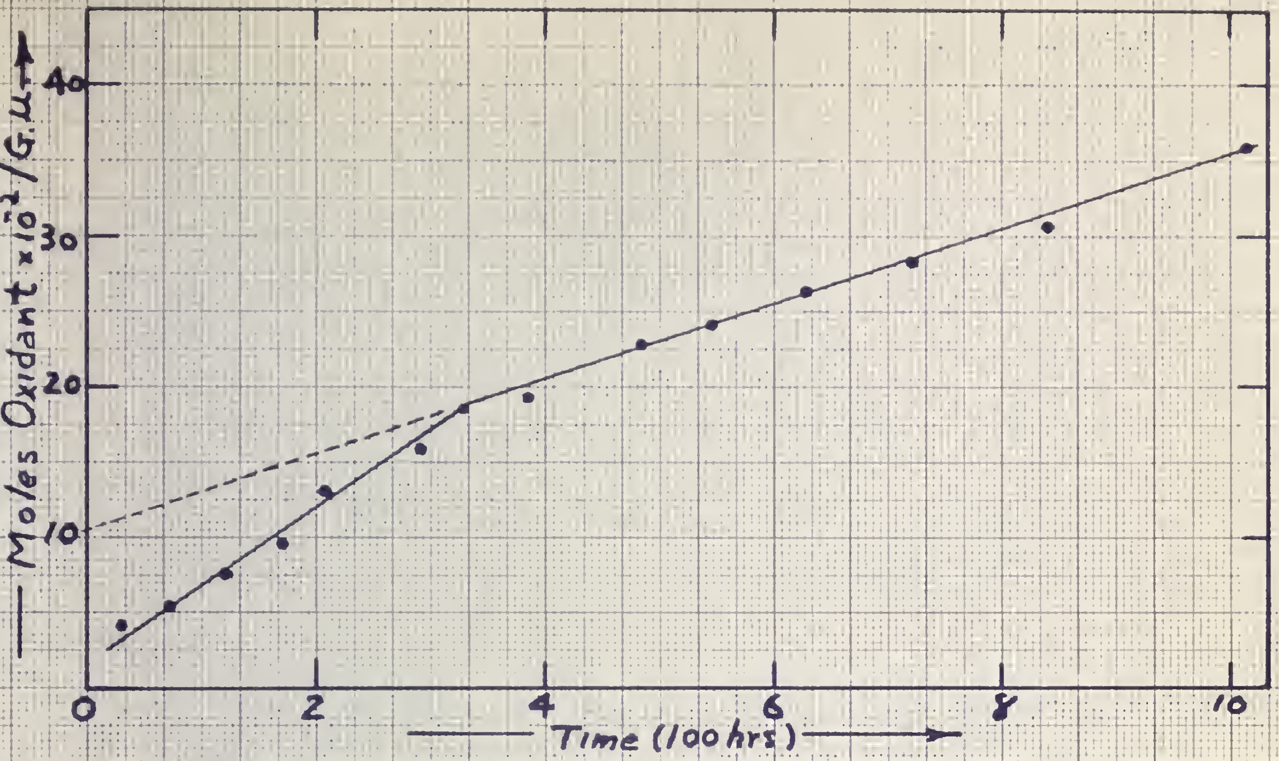


Fig. 12a $Pb(OAc)_4$ oxidation of sample T-75-1

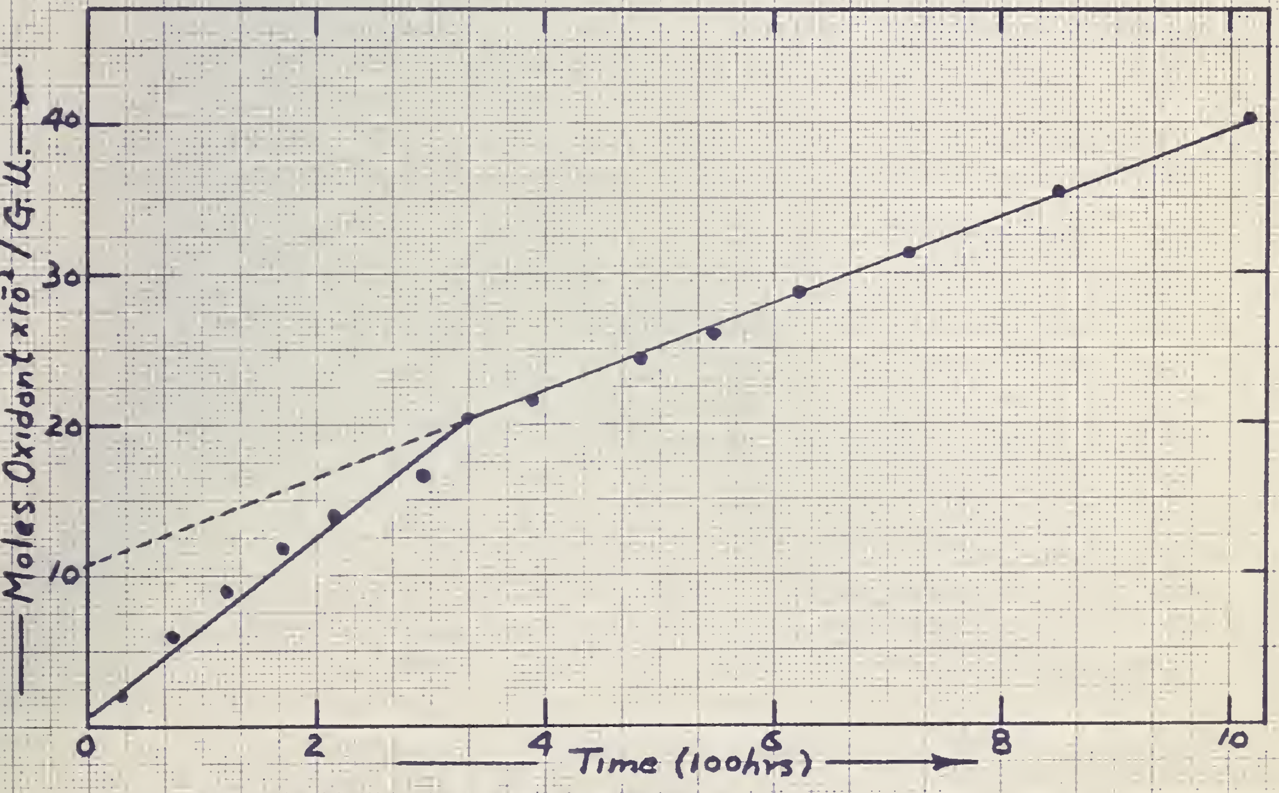


Fig. 12b of T-75-5

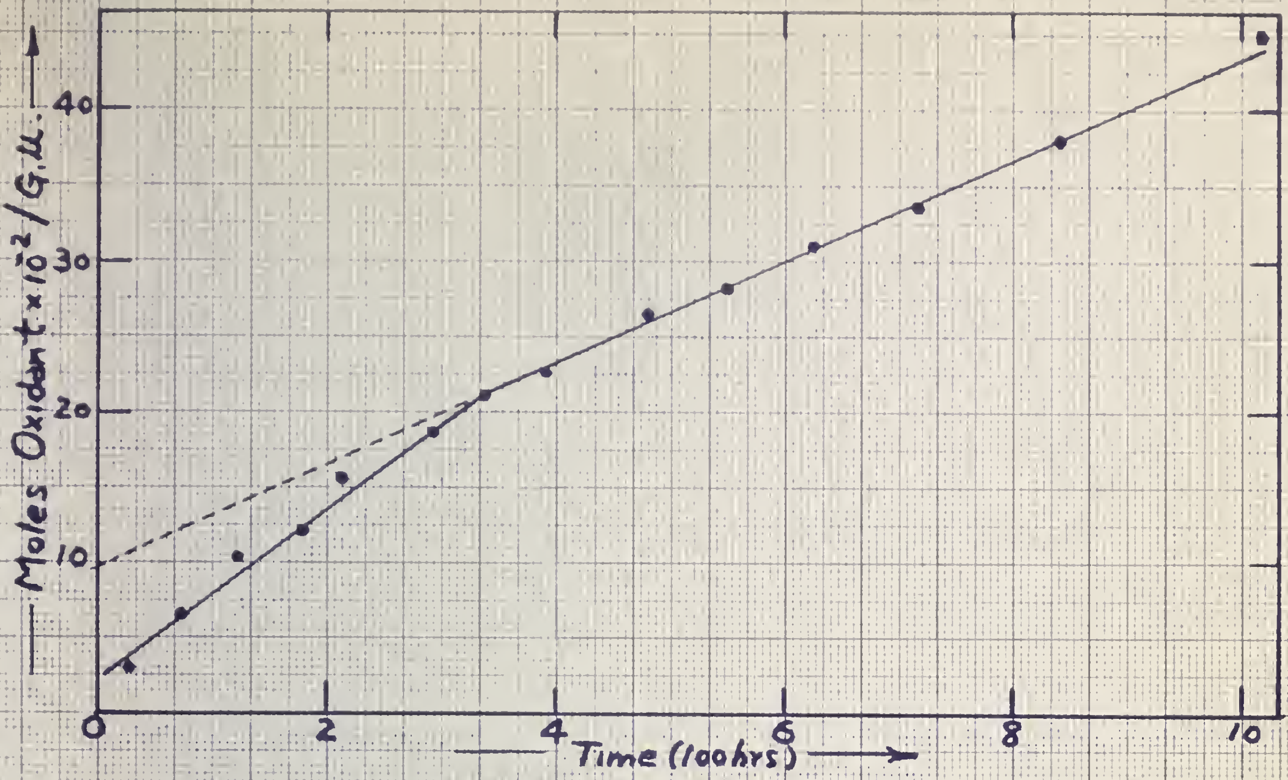


Fig. 13a Pb(OAc)$_4$ oxidation of sample T-S-1

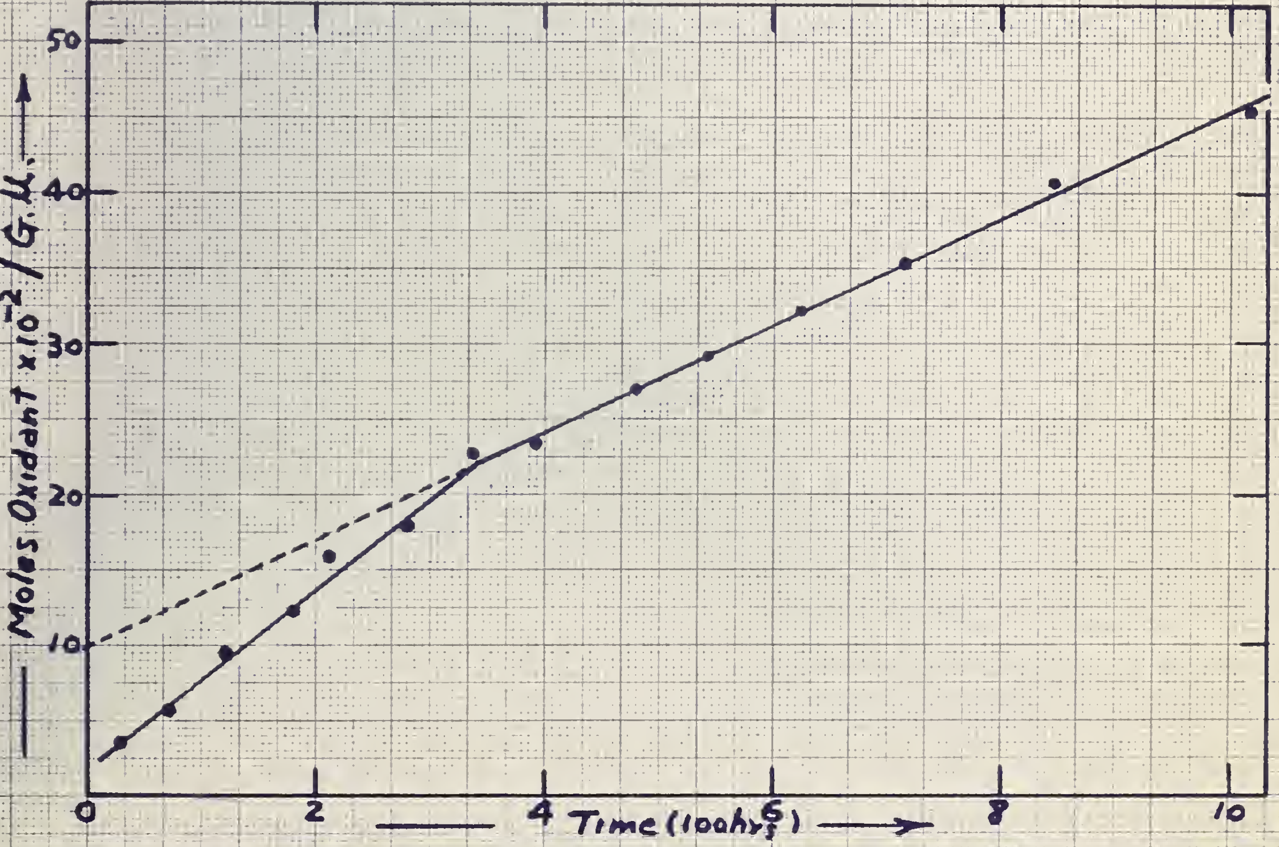


Fig. 13b of T-S-5

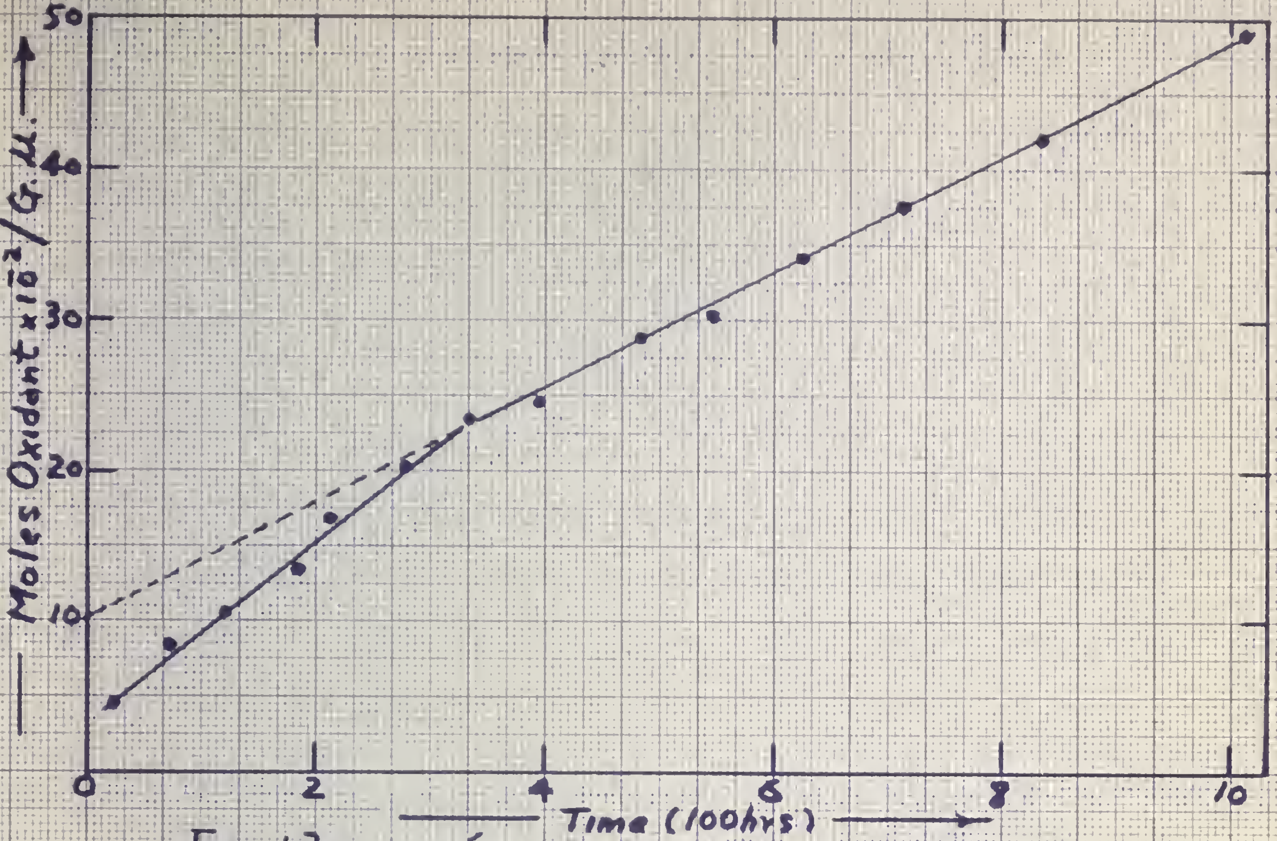


Fig. 13c of T-S-11

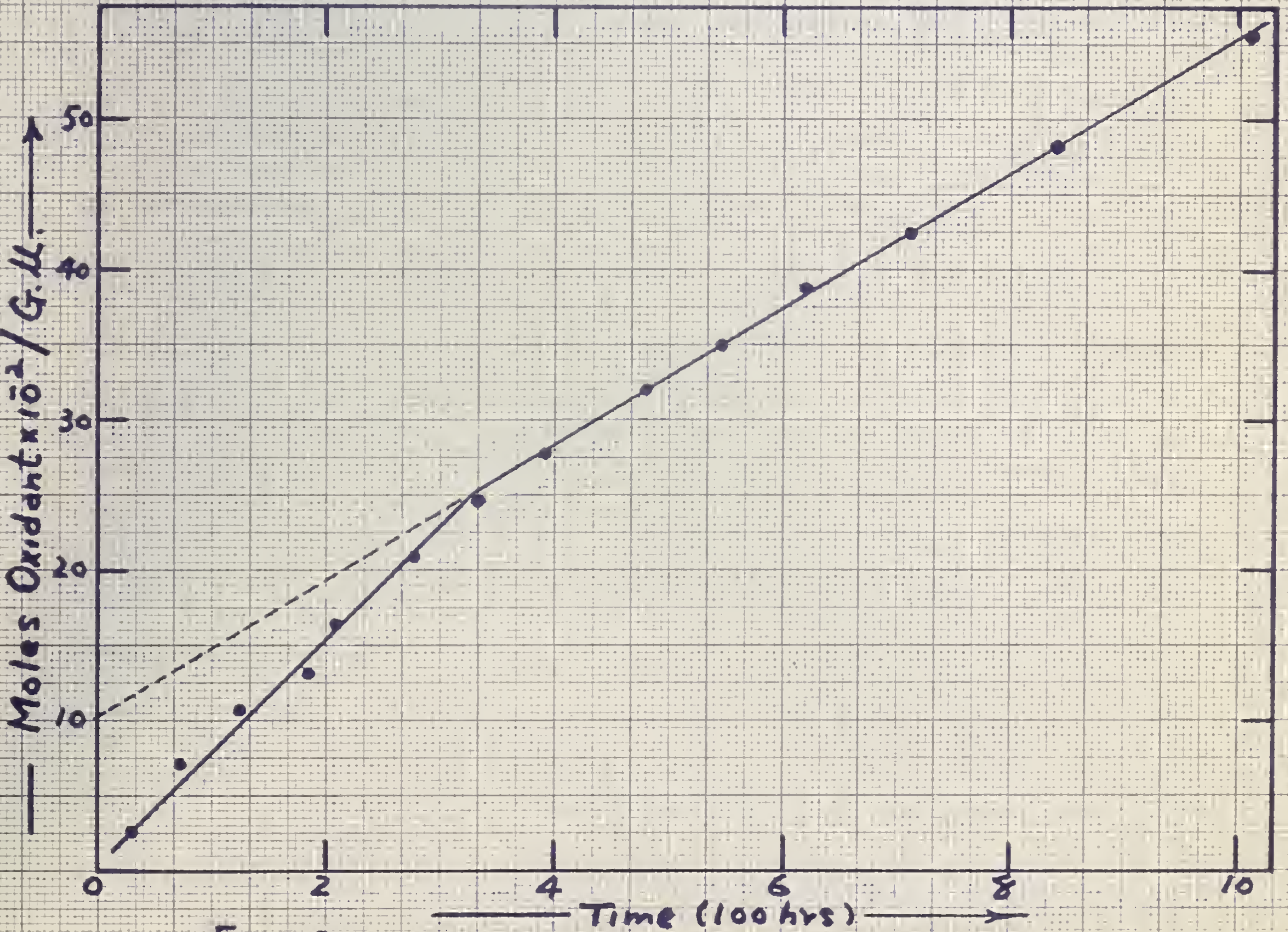


Fig. 13d of T-S-15

For series T-0, the data show a continuous decrease in the consumption of lead tetraacetate by the nitrates with increase of wetting and drying cycles (Table 15, Col. 2). The nitrogen analyses (Table 7, Col. 2) for the series reflect a gradual and corresponding increase in reactivity. Since consumption of oxidant by a nitrocellulose sample should decrease with increased degree of substitution of the secondary hydroxyls, the nitration and oxidation results seem to agree with each other and indicate the fact that alternate wetting and drying process at 0° leads to the increasing ease of nitration at the glycol units of the cellulose molecule. It is also to be noted that at this wetting temperature of 0° both the changes in degree of nitration (10.20% to 10.61% N, p. 63) and the consumption of lead tetraacetate (11.3×10^{-2} to 9.5×10^{-2} moles per anhydroglucose unit, p. 69) are the greatest among all the series investigated.

In series T-50, T-75, T-S (Table 15, Col. 4,5,6), the results are just the reverse, i.e. increase of lead tetraacetate consumption accompanies the increase of wetting and drying cycles. This is again in good correlation with the corresponding nitration data (Table 7, Col, 4,5,6), all of which show a gradual decrease of reactivities toward the technical nitrating acid. Therefore, it may be concluded that at wetting temperatures of 50°, 75° and in steam, the cyclic process leads to the decrease in degree of nitration at the glycol units.

The harmonious correlations exhibited by the oxidation and nitration data in the above four series is not present for the linters wetted at 25° i.e. the T-25 series (Table 15, 7, Col. 3). In this case, both the consumption of the oxidant and the degree of nitration show definite and distinct increments with the increase of wetting and drying cycles. The apparent discrepancy seems to indicate that the increasing ease of total degree of nitration is accompanied by the gradual decrease of accessibilities of the glycols in the anhydroglucose units.

The consumption of lead tetraacetate by cellulose nitrate of zero wetting sample should also be noted. The figure of 6.7×10^{-2} moles (Table 15, p.69) of oxidant compared to the higher values for the wetted and dried samples is surprisingly low and indicates the presence of a relatively small amount of free glycols in zero wetting nitrocellulose sample. This is remarkable since the total degree of nitration (10.36% N) is comparable with that for the other remaining nitrates.

With the limited data available, no satisfactory explanation can be suggested for the discrepancies which occurred in T-25 series and the zero wetting sample with respect to their total degree of nitrations and the corresponding lead tetraacetate consumptions. However, when the results are further analysed with the aid of some statistical approach, a much clearer picture will be obtained (refer to p. 94).

To determine the distribution of nitrate groups in partially nitrated cellulose, Murray and Purves (26)

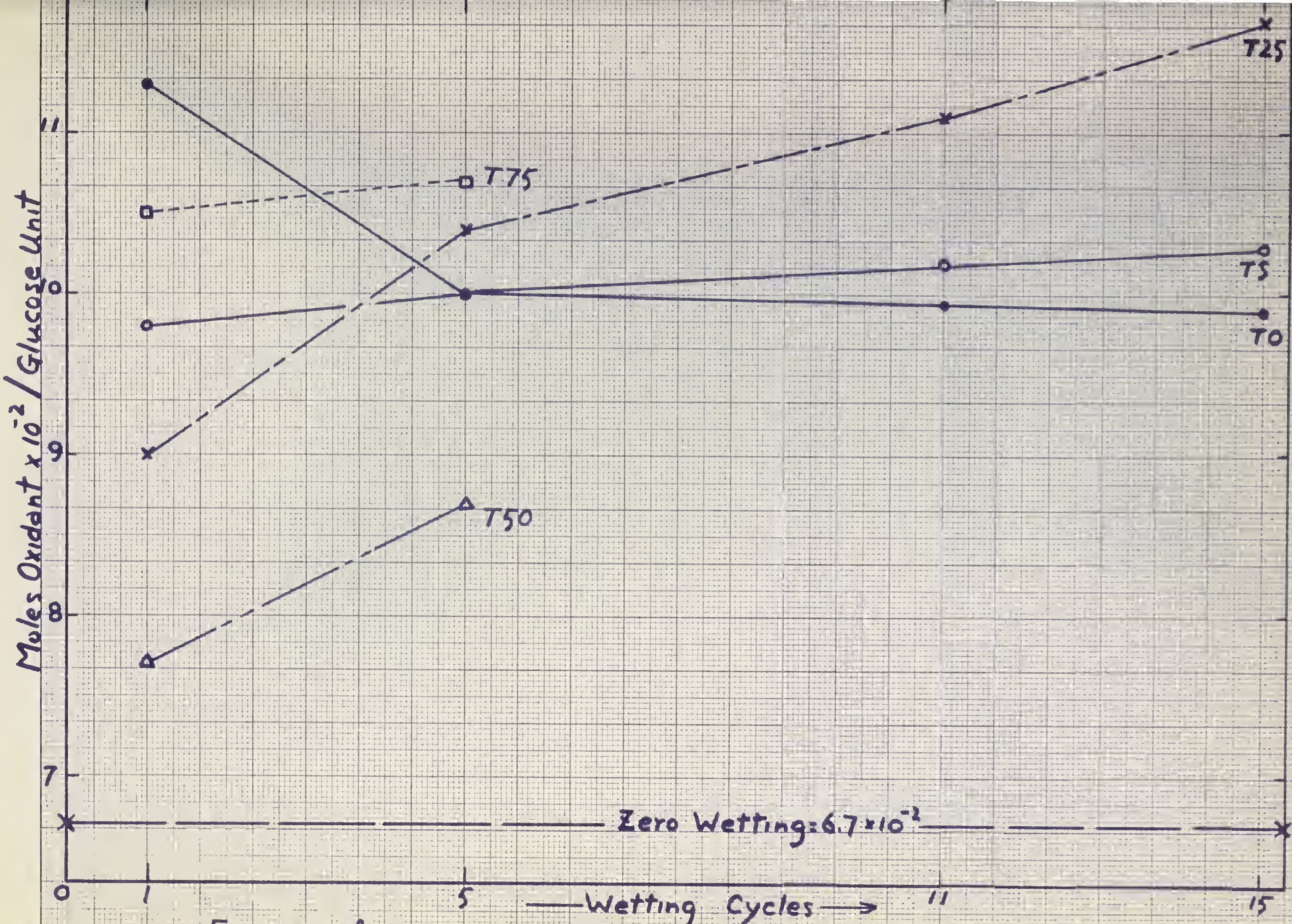


Fig. 14 A summary on the consumptions of $Pb(OAc)_4$ by nitrocellulose sample series T

employed sodium iodide to replace primary nitrate groups with iodine, a method found to be applicable in the case of simple sugar derivatives. However, they reported that for highly nitrated cellulose (13.2% N), the method was unsatisfactory owing to the oxidative side reactions. On treatment of other nitrocelluloses (2.5 to 7.5% N) with sodium iodide (26), the results indicated that at least one half of the nitrate groups are in the primary position.

Two of the main factors which determine the above distribution of substituents are the kinetics of the reaction and the nature of esterification itself. There are only three possibilities with respect to the relative rates of reaction of the primary and secondary hydroxyls; the former being much faster than the latter, or vice versa, or the two are equally reactive. However, it should be pointed out that the over all rate of nitration is fairly rapid and the reaction is complete within a period of ten minutes (54). Therefore in the present case, with a nitration period of half an hour, an equilibrium of reaction should be thoroughly established for both the primary and secondary hydroxyls. We are thus concerned with the state of affairs wherein the relative rates of reaction of the primary and secondary hydroxyls are not the determining factors in distribution of substituents. What seems important is the position of equilibrium and the accessibility of the hydroxyls to the reagent.

As to the nature of nitration, in fact, the nature of all etherifications and esterifications of cellulose, only three possibilities could exist (36,55). One is the

viewpoint that the hydroxyl groups are randomly substituted. If the fibrous structure of cellulose has been sufficiently swollen or dispersed by a suitable environment, it should, ideally, expose all portions of the macromolecule uniformly to the reagent. In this case, the free hydroxyl groups (and also the substituted ones) would be scattered at random but with uniform average density throughout the length of the cellulose chain. If the second carbon position contained X free hydroxyl groups and the third positions H-X, where H is the sum of the unsubstituted secondary hydroxyl groups, then the probability that a given glucose residue remains unnitrated in both positions would be $X(H-X)$. This product will not decrease quickly from the maximum of $\frac{H^2}{4}$ until X becomes small compared to $\frac{H}{2}$ which is unlikely with random substitution.

Another possible assumption is that substitution in either the second or third position will greatly depress the reactivity of the adjacent hydroxyl group in the same glucose unit. In this case, no unsubstituted glycol will occur until the amount of free hydroxyl groups distributed between the two positions, i.e. H, exceeds one mole. In cellulose nitrates of relatively low nitrogen content, H naturally lies between one and two moles and the probability of the glycol coincidence would be $X + (H-X) - 1$ or $H - 1$.

The third possibility concerning the mode of nitration is that the readily accessible regions in the fibers will be easily and extensively substituted. The

hydrophobic shell so formed then hinders the progress of the reaction to the interior of the micelles. Such a highly heterogeneous mechanism would tend to produce a partly substituted cellulose in which the glucose residues are either completely substituted or completely unsubstituted. The corresponding probability of glycol groupings will be $\frac{H}{2}$.

In short, the above three assumptions can be summarized and expressed in terms of methematical forms (36, 55) as:-

1. Homogeneous reaction theory,- corresponding glycol occurrence is $\frac{H^2}{4}$.
2. Depressive reaction theory,- glycol coincidence is H-1.
3. Heterogeneous reaction theory,- glycol occurrence is $\frac{H}{2}$.

Where H is the total number of secondary hydroxyls unnitrated,

Let F denote the total number of free hydroxyls, both primary and secondary,

and G represent the number of free glycols, i.e. number of free secondary hydroxyls as glycols.

Both F and G can be derived from the data collected in nitrogen analyses of the nitrocellulose samples and the lead tetraacetate oxidation of the corresponding nitrates. F equals to 3-D, D being the degree of nitration in terms of hydroxyls substituted (see Table 8, p.64). This is listed in Table 16(p. 37). G is simply the consumption of the oxidant per anhydroglucose unit (Table 15), for

easy reference, it is again shown in Table 17, p. 87). Equating C with $\frac{H^2}{4}$, H-1, and $\frac{H}{2}$ according to the assumptions #1, #2 and #3 respectively, H can be found. They represent the total number of secondary hydroxyls unsubstituted and are listed in Table 18, 19 and 20(p. 88). The corresponding number of primary hydroxyls unnitrated will then be calculated from F-H and appear in Table 21, 22 and 23 (p. 89).

With the results thus obtained, the distribution of the nitrate groups at the primary and secondary positions will be obvious. These are presented in Table 24 and 25 (p.90) for assumption #1, Table 26 and 27 (p. 91) for #2, Table 28 and 29 (p. 92) for assumption #3 respectively. In the second last Table, (i.e. Table 28) more than half of the values are negative. This indicates the number of primary hydroxyls nitrated to be less than zero which is clearly unreasonable. Therefore it is justified to conclude that the mode of nitration is not heterogeneous in nature. This conclusion seems to agree with the overwhelming mass of results related to this subject (56).

Although the distribution chart derived from the depressive reaction theory (Table 26 and 27) exhibits reasonable degrees of nitration for both the primary and secondary hydroxyls, with the former having about twice as much reactivity as the latter, yet when the relative space factors of a nitro group and an anhydroglucose unit are considered, little evidence exists to support such a theory. With the conformational structure of cellulose

TABLE 16

Total Number of Free Hydroxyls F (Moles/G.U.)*

Wetting Cycle	Wetting Series T-0	T-25	T-50	T-75	T-S
0	1.201				
1	1.242	1.219	1.133	1.129	1.207
5	1.174	1.193	1.237	1.166	1.232
11	1.140	1.161			1.244
15	1.135	1.156			1.252

* In this and the rest of the Tables, G.U. stands for glucose unit.

TABLE 17

Number of Free Glycols G (Moles/G.U.)
i.e. Free Secondary Hydroxyls as Glycols

Wetting Cycle	T-0	T-25	T-50	T-75	T-S
0	0.067				
1	0.113	0.090	0.0775	0.105	0.093
5	0.100	0.104	0.087	0.107	0.100
11	0.0975	0.111			0.102
15	0.095	0.117			0.103

TABLES OF

TOTAL NUMBER OF FREE SECONDARY HYDROXYLS (Moles/G.U.)

Table 18 Based on Assumption #1, i.e. Random Substitution

Wetting Cycle	T-0	T-25	T-50	T-75	T-S
	Wetting Series				
0	0.5177				
1	0.6723	0.6003	0.5558	0.6480	0.6062
5	0.6305	0.6451	0.5799	0.6540	0.6395
11	0.6246	0.6564			0.6392
15	0.6165	0.6241			0.6410

Table 19 Based on Assumption #2, i.e. Progressive Substitution

Wetting Cycle	T-0	T-25	T-50	T-75	T-S
	Wetting Series				
0	1.067				
1	1.113	1.090	1.073	1.105	1.098
5	1.100	1.104	1.037	1.107	1.100
11	1.098	1.111			1.102
15	1.095	1.117			1.103

Table 20 Based on Assumption #3, i.e. Heterogeneous Substitution

Wetting Cycle	T-0	T-25	T-50	T-75	T-S
	Wetting Series				
0	0.134				
1	0.226	0.130	0.155	0.210	0.196
5	0.200	0.203	0.174	0.214	0.200
11	0.195	0.222			0.204
15	0.190	0.234			0.206

TABLES OF

NUMBER OF FREE PRIMARY HYDROXYLS F-F (Moles/G.U.)

Table 21 Based on Assumption #1, i.e. Random Substitution

Wetting Cycle	Wetting Series T-0	T-25	T-50	T-75	T-S
0	0.6833				
1	0.5697	0.6137	0.6312	0.4810	0.5808
5	0.5415	0.5479	0.6471	0.5118	0.5995
11	0.5154	0.4946			0.6051
15	0.5185	0.4719			0.6101

Table 22 Based on Assumption #2, i.e. Depressive Substitution

Wetting Cycle	Wetting Series T-0	T-25	T-50	T-75	T-S
0	0.134				
1	0.129	0.129	0.110	0.024	0.109
5	0.074	0.039	0.150	0.059	0.132
11	0.042	0.050			0.142
15	0.040	0.039			0.149

Table 23 Based on Assumption #3, i.e. Heterogeneous Substitution

Wetting Cycle	Wetting Series T-0	T-25	T-50	T-75	T-S
0	1.067				
1	1.016	1.039	1.033	0.919	1.011
5	0.974	0.985	1.063	0.952	1.032
11	0.945	0.939			1.040
15	0.945	0.922			1.046

TABLE 24

Number of Primary Hydroxyls Nitrated 1-(F-H) Moles/G.U. Based on Assumption #1

Wetting Cycle	Wetting Series				
	T-0	T-25	T-50	T-75	T-S
0	0.3167				
1	0.4303	0.3813	0.3683	0.5190	0.4192
5	0.4585	0.4421	0.3529	0.4832	0.4005
11	0.4846	0.5054			0.3949
15	0.4315	0.5231			0.3899

TABLE 25

Total Number of Secondary Hydroxyls Nitrated (2-H) Moles/G.U. Based on Assumption #1

Wetting Cycle	Wetting Series				
	T-0	T-25	T-50	T-75	T-S
0	1.482				
1	1.323	1.400	1.443	1.352	1.374
5	1.363	1.355	1.410	1.346	1.363
11	1.375	1.334			1.361
15	1.334	1.316			1.358

TABLE 26

Number of Primary Hydroxyls Nitrated 1-(F-H) Moles/G.U. Based on Assumption #2

Wetting Cycle	Wetting Series T-0	T-25	T-50	T-75	T-S
0	0.866				
1	0.871	0.871	0.890	0.976	0.891
5	0.926	0.911	0.850	0.941	0.868
11	0.960	0.950			0.858
15	0.996	0.961			0.851

TABLE 27

Total Number of Secondary Hydroxyls Nitrated (2-H) Moles/G.U. Based on Assumption #2

Wetting Cycle	Wetting Series T-0	T-25	T-50	T-75	T-S
0	0.933				
1	0.887	0.910	0.922	0.895	0.902
5	0.900	0.896	0.913	0.893	0.900
11	0.902	0.889			0.898
15	0.905	0.883			0.897

TABLE 28

Number of Primary Hydroxyls Nitrated 1-(F-H) Moles/G.U. Based on Assumption #3

Wetting Cycle	Wetting Series T-0	T-25	T-50	T-75	T-S
0	-0.067				
1	-0.016	-0.039	-0.033	0.081	-0.011
5	0.026	0.015	-0.063	0.048	-0.032
11	0.055	0.061			-0.040
15	0.055	0.078			-0.046

TABLE 29

Total Number of Secondary Hydroxyls Nitrated (2-H) Moles/G.U. Based on Assumption #3

Wetting Cycle	Wetting Series T-0	T-25	T-50	T-75	T-S
0	1.866				
1	1.774	1.820	1.845	1.790	1.804
5	1.800	1.792	1.826	1.786	1.800
11	1.805	1.773			1.796
15	1.810	1.766			1.794

in mind (63), the pyranose ring of the anhydroglucose unit exists in chair form with minimum strain, the two secondary hydroxyls stretch outward equatorially from the mean plane but in different directions. Since the attacking nitro group is planar and relatively small in molecular size, it seems very unlikely that the substitution of one hydroxyl group would depress the accessibility of the other.

The overwhelming portion of evidence (56) favors the homogeneous theory of cellulose nitration. The conclusion based on the fact that an equilibrium exists between the nitrating medium and the nitrocellulose over a large range of composition, and the final nitrogen content is independent of the reaction time after equilibrium is established. The existence of this equilibrium is in harmony with the homogeneous theory of nitration only. The distribution of the nitrate groups, based on this theory, at the primary and secondary positions is shown on page 90 (Table 24 and 25, p.90)(Fig. 15 and 16, p.95-6. It is interesting to note that the over all progressive ease of nitration for T-0 series with the wetting and drying cycles (Table 7. p. 63) appears to arise from the increase of reactivities of both the primary and the secondary hydroxyls; just as the over all decrease of nitration for T-50, T-75 and T-S series caused by the progressive decline of reactivities of both types of hydroxyls. However, the T-25 series seems to possess a different picture, the accessibilities at the primary positions increase gradually with a corresponding decay of reactivity at the secondary positions, although

the overall degree of nitration increases with the progress of the cycles. This falls in line to the previous observations (p.62) that the overall rise of reactivity for T-25 series is comparatively milder than that found in the T-0 series since in the former case, the decline in reactivity of the secondary hydroxyls toward nitration would overshadow part of the increase in reactivity at the primary positions.

Furthermore, when the degrees of nitration at the primary and secondary hydroxyls for the zero wetting sample are studied (p. 90), the primary one is relatively lower (0.317 OH) and the secondary higher (1.48 OH) than the corresponding others. This shows that the partially swollen state caused by the 'dewaxing process' of the cotton linters produces greater ease of accessibility to the secondary hydroxyls rather than to the primary, and clarifies the apparent discrepancy noted previously (p. 81).

The most significant feature noticeable in the homogeneous theory is that the accessibility of the secondary hydroxyls is about twice that of the primary ones toward nitration. (Compare the figures in general in Table 24 and 25). Although this seems contrary to most of the evidences collected from the studies of acetylation, methylation, and carboxymethylations of cellulose, however, the results may not be applicable to nitration. Recently, Timell studied the influence

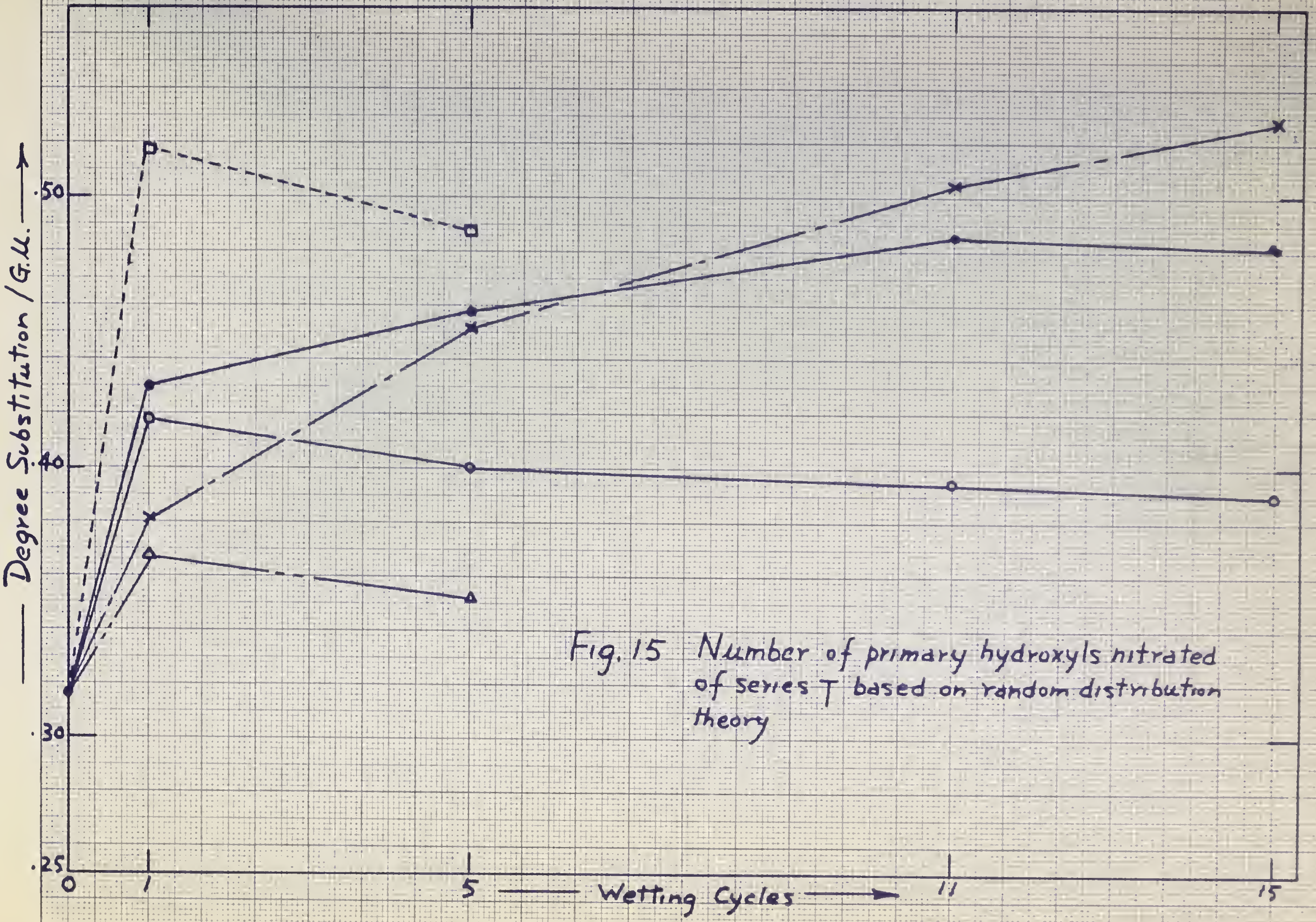


Fig. 15 Number of primary hydroxyls nitrated of series T based on random distribution theory

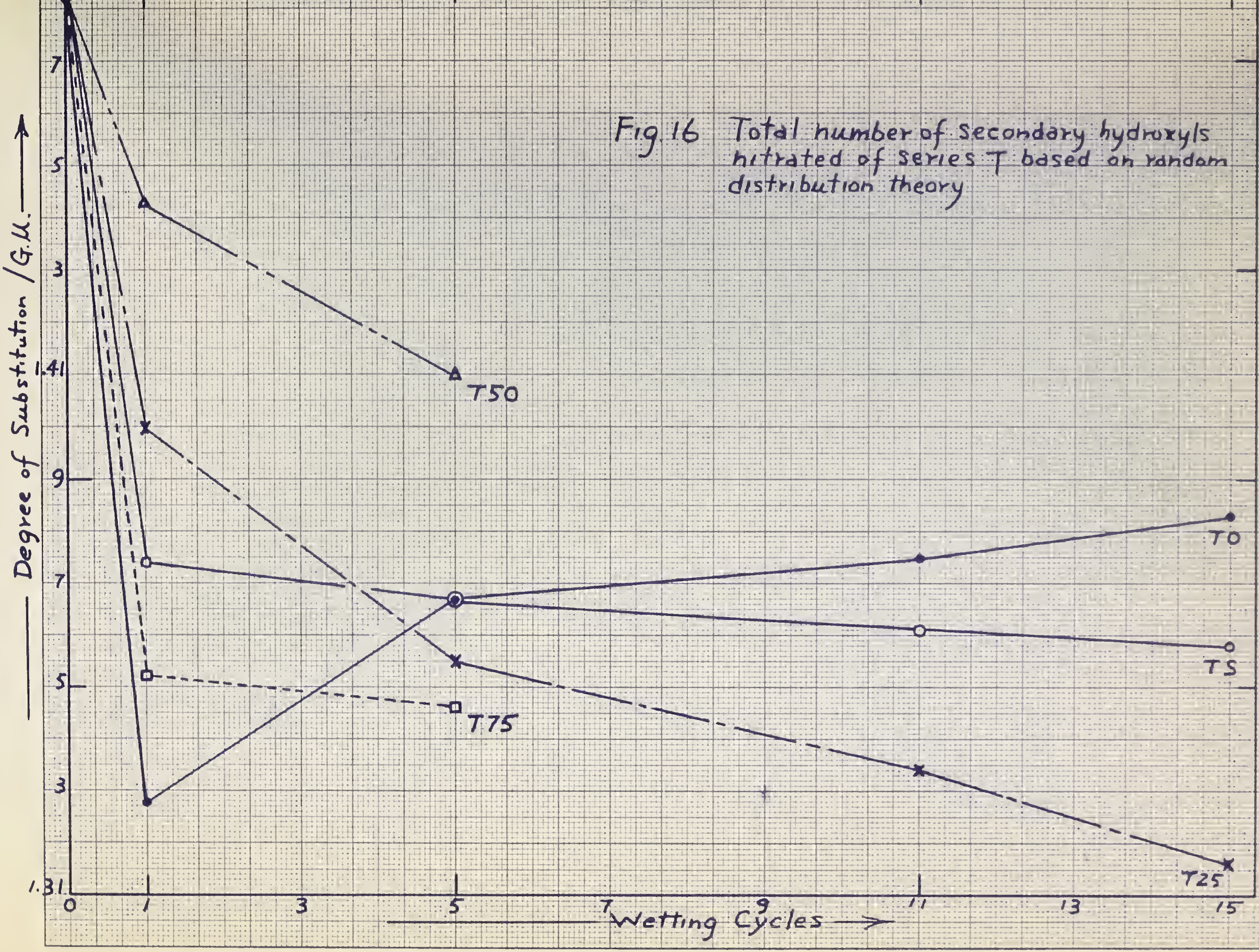


Fig. 16 Total number of secondary hydroxyls nitrated of series T based on random distribution theory

HUGHES OWENS 315M-METRIC

of fiber structure on the nitration of native cellulose (57). He reported that nitrates are more highly substituted in the interior of the microfibrils and along the longer chain molecules than on the surface or along the shorter chains, that is, nitration is exactly opposite to what is typical of other partially substituted cellulose reactions. It appears to involve an initial rapid but only partial esterification of the surface of the fibers, followed by a slower but more thorough conversion of the interior. It is assumed that only the planar nitric acid molecules can enter the inner crystalline regions resulting in a relatively higher degree of nitration there.

Though the report (57) did not actually state a reversal of the accessibilities of primary and secondary hydroxyls towards nitration, nevertheless, it is encouraging enough to note that the mode of nitration is very much different from other esterifications.

To study more carefully the results obtained by Murray and Purves (26) on the distribution of nitrate groups in partially nitrated cellulose, it is noted that despite the apparent loss of nitrate groups during iodination of the nitrocelluloses, the overall iodine replacement of nitro groups keeps a rather steady 50% (i.e. 50% of the nitro groups are at the primary positions) for samples containing 2 to 7.5% N, but gradually decreases to 42% for samples of 9.0% N. This indicates the relative ease

of nitration at the secondary positions as the total degree of substitution is increased. Unfortunately, no comparable information is available from their paper (26) concerning the nitrates with nitrogen content of 10 to 11% to verify or contradict our findings.

Although it has been clearly noted that tosyl groups at the secondary positions slowly participate in iodine replacement reactions (37, 38, 58, 59), however, the complication does not seem detectable unless the iodination period exceeds six hours (37). It was suggested (38) that by maintaining identical reaction conditions throughout, the method of tosylation followed by iodination is still applicable to the detection of differences in reactivities of cellulose samples of varied past histories. With such a recommendation in mind, this standard procedure which has been repeatedly employed to differentiate the accessibilities of primary and secondary hydroxyls, is being used in this project.

Cellulose samples of series I and II were tosylated and iodinated under identical conditions (see Experimental page 52), series II being subjected to these reactions three months after those for series I had been completed. During tosylation, the solution of p-toluenesulfonyl chloride in pyridine appeared light reddish in color and upon addition of this to the flasks containing different cellulose samples in pyridine, the intensity of the coloration did not seem to alter and remained unchanged throughout the reaction period. The samples thus tosylated when suitably

washed and extracted, showed a very faint yellowish color.

Portions of the extensively dried samples of tosylated cellulose were analysed for their sulphur content (p. 55) Tables 30 and 31 (p.100 to 101) give the values in % S by weight with the corresponding number of tosyl groups introduced recorded in column 3. The results from the two series show reasonable agreement in their general degree of substitutions despite the fact that they underwent entirely separate but almost identical treatments right from the beginning of dewaxation.

During sulphur analyses, the precipitate of barium sulphate was in such a finely divided state that No. 40 quantitative filter paper did not retain it entirely. It was found necessary to use Gooch crucibles with a relatively thick mat of asbestos to give a clear filtrate. With this adjustment, the duplicates for most of the samples were very close and the six blanks carried out at separate intervals showed no corrections to be necessary.

From the data (p. 100), wetting and drying of the cellulose samples at 25° exhibit a gradual decrease in their total degree of substitution for tosylation as the cycles proceed. In order to check whether there was any loss of the tosyl groups during extraction with methyl alcohol (p. 101), sample II-0 was divided into two parts after it had been tosylated and thoroughly washed; one part (II-0-A) was extracted with the reagent as usual and the other (II-0-B) without. Their resulting sulfur contents are listed on the first two lines of column 2 of Table 31(P·101).

TABLE 30

Tosylation of Cellulose Samples Alternately Wetted and Dried*

Series I Wetted at 25 ± 0.1° C

(1) Wetting Cycle	(2) S%	(3) Calculated total OH group tosylated (from S%)	(4)** Calculated total OH group tosylated (from S% & I%)
0	2.60	0.150	0.134
1	2.39	0.137	0.124
5	2.53	0.148	0.135
11	2.21	0.125	
15	2.18	0.123	0.103

* Composition of the reaction mixture:

Cellulose 2.5 gm. (0.1623 mole per liter)
Tosyl chloride 29.4 gm. (1.623 mole per liter)
Pyridine 95 ml.

** Column (4) of Table 30 is the sum of columns (4) and (6) of Table 32.

TABLE 31

Tosylation of Cellulose Samples Alternately Wetted and Dried[a]

Series II Wetted at 25 ± 0.1° C.

(1) Wetting Cycle	(2) S%	(3) Calculated total OH group tosylated (from S%)	(4)[b] Calculated total OH group tosylated (from S% to I%)
C-A[c]	8.53	0.146	0.139
C-B	8.57	0.149	0.139
1	8.46	0.141	0.142
5	8.29	0.130	0.130
11	8.56	0.143	0.137
15	8.16	0.132	0.111

[a] Tosylated three months after series I had been completed but under identical conditions except the omission of methanol extraction.

[b] Column (4) of Table (31) is the sum of Columns (4) and (6) of Table 33.

[c] Methanol extraction was included.

They agree with each other within experimental error, indicating the suspicion to be invalid. However, before this conclusion was reached, a side investigation was undertaken concurrently. Methyl cellulose of 12.9% methoxy content by weight (average) was prepared from chemically reactive cellulose (Experimental p. 31) according to the procedures outlined by Rosenthal (60). It was then iodinated under identical conditions as before and analysed for its iodine content. The result showed quantitative replacement of the methoxy groups by iodine. But, this problem did not receive any further investigation since the tosyl groups were found unreplaced during methyl alcohol extraction. This interesting discovery will receive further attention at a later date.

The tosyl cellulose samples were then iodinated for four hours only to minimize any complication which might occur by the participation of secondary tosyl groups (see also Experimental p. 54 in general). The light yellow color of acetonyl-acetone containing sodium iodide and heated to 110° intensified slightly. The color intensities gradually increased when the tosyl cellulose samples were added but did not turn reddish as noted by some of the previous workers (37). When washed and extracted, the iodinated samples were dried over phosphoric anhydride in vacuum as usual before sulphur and iodine analyses.

The results are shown in Tables 32 and 33 (p.103 and 104). Columns 2 and 3 list the individual iodine and

TABLE 32

Combined Iodine and Sulfur Analyses on Tosylated Cellulose Followed by Iodination

Series I wetted at 25 ±0.1°C

(1) Wetting Cycle	0	1	5	15
(2) I%	6.83	6.80[b]	6.65	6.11
(3) S%	0.680	0.533	0.741	0.354
(4) Calculated Primary OH Substituted per G.U.[a]	0.0961	0.0948	0.0937	0.0839
(5) Calculated Free Primary OH per G.U.	0.9039	0.9052	0.9063	0.9161
(6) Calculated Secondary OH Substituted per G.U.	0.0379	0.0295	0.0413	0.0192
(7) Calculated Free Secondary OH per G.U.	1.9621	1.9705	1.9587	1.9808

[a] G. U. = glucose unit

[b] Individual Values 6.73% and 6.86%

TABLE 33

Combined Iodine and Sulfur Analyses on Tosylated Cellulose Followed by Iodination

Series II Wetted at 25 ± 0.1°C

(1) Wetting Cycle	OA*	OB*	1	5	11	15
(2) I%	6.19	6.17	6.53	5.37	5.75	4.62
(3) S%	0.921	0.921	0.881	0.844	1.01	0.845
(4) Calculated Primary OH Substituted per G.U.	0.0875	0.0874	0.0925	0.0826	0.0805	0.0642
(5) Calculated Free Primary OH per G.U.	0.9125	0.9126	0.9075	0.9174	0.9195	0.9358
(6) Calculated Secondary OH Substituted per G.U.	0.0517	0.0516	0.0495	0.0471	0.0565	0.0465
(7) Calculated Free Secondary OH per G.U.	1.9483	1.9484	1.9505	1.9529	1.9435	1.9535

* OA with and OB without methanol extraction.

sulphur contents from analyses. With appropriate conversion factors (p.59), they are shown respectively as the number of primary and secondary hydroxyls substituted. These values are listed in columns 4 and 6. It is then simple to calculate the corresponding number of free primary and secondary hydroxyls which are shown in Columns 5 and 7. The sum of Columns 4 and 6 for each sample represents the total degree of substitution which should be equal to the value previously found from the sulfur content alone on the corresponding tosylated sample. By comparing the last two columns on Tables 30 and 31 (p. 100 and 101), they seem to show that the calculated sum (column 4 of Tables 30 and 31) usually give lower values than the ones found by sulfur contents of the tosylated but uniodinated samples (Column 3 of Tables 30 and 31). However, the divergence is not too serious, in fact better than the similar results reported in the literature (33). It should also be noted that the values are obtained from samples which have undergone two different reactions and three separate analyses, a process which would inevitably accumulate some experimental errors.. To investigate this discrepancy and to assure ourselves that the iodine analyses were not in error, iodinated tosyl cellulose samples of II - 1 and II - 5 were analysed for their iodine contents by both potentiometric titration (61) and ordinary wet gravemetric method (62). The results thus obtained are in very good agreement with those from the previous sodium thiosulphate titrations.

Both series I and II show a gradual decline of

iodine and sulfur contents with the increase of wetting and drying cycles. This indicates that at 25° wetting both the primary and secondary hydroxyls become less reactive towards the reagent tosyl chloride as wetting and drying of cellulose is repeated. When the actual values are compared, the cyclic process seems to affect both the primary and secondary hydroxyls to a similar extent without any significant preference.

Portions of cellulose samples series III which had undergone wetting only once at different temperatures (see Experimental p. 32) were tosylated and iodinated as inthe case of series I and II. Table 34 on p. 108 shows the sulfur contents of the tosyl cellulose samples and the corresponding total degree of substitution. Table 35 (p. 109) gives the sulfur and iodine analyses of the iodinated tosyl samples with the corresponding calculated number of primary and secondary hydroxyls substituted.

Although no significant trends of change in the reactivity are apparent, however, it is interesting to note that the total degree of substitution seems to reach a maximum of 0.0397 glucose unit for 25° wetting (p. 108) at higher and lower wetting temperatures, there seem to exist a continuous decline of the reactivities.

Referring to the sulfur and iodine analyses in Table 35 (p. 109) a similar phenomenon persists. For the corresponding primary hydroxyls, a maximum seems to occur along the 25° - 75° range, and with the secondary hydroxyls, the maximum exists between 25° - 50° interval. Since only

one wetting cycle had been performed on the cellulose samples, the data is not conclusive and no definite indications can be suggested. Nevertheless, the result does show that wetting and drying process influences the reactivities of the cellulose molecules at both the primary and secondary positions. Furthermore, here again it is notable that when cellulose is wetted in steam, the resulting sample in the lumpy and collapsed state exhibits a drop in its accessibilities at both the primary and secondary hydroxyls toward such bulky reagent as tosyl chloride.

In an attempt to compare and to correlate, if possible, the results thus obtained from the nitration and tosylation - iodination data, two tables have been set up (p.111 to 112). However it must be pointed out that the cellulose samples given the two reactions have been separately although identically pretreated; moreover, the overwhelming bulk of evidence available at present tends to classify the mode of nitration as homogeneous or permitoid in nature (56), whereas the tosylation reaction is believed to be heterogeneous (36). Hence the comparison of the results from the two different reactions may not be valid.

Table 36 on p. 111 gives the values obtained from nitration series T-25 and tosyl-iodination series II. Column 1 denotes the wetting cycles, 2 and 3 show the total number of hydroxyls nitrated and tosylated at 25° respectively, 4 and 5 give the number of primary hydroxyls substituted, whereas the last two columns indicate the total degree of

TABLE 34

Tosylation of Cellulose Samples Wetted Once Only*

Series DT Wetted at Different Temperatures

(1) Wetting Temperature	(2) S%	(3) Calculated Total OH group tosylated (from S%)	(4) Calculated Total OH group tosylated (from S% and I%)
No wetting	1.26	0.0679	0.0661
0°	1.58	0.0864	0.0731
25 ± 0.1	1.63	0.0897	0.0817
50 ± 2	1.58	0.0864	0.0822
75 ± 2	1.57	0.0857	0.0746
steam	1.35	0.0730	0.0673

* Composition of the reaction mixture

Cellulose	2.5 gm.	(0.1623 mole per liter)
Tosyl Chloride	23.5 gm.	(1.298 mole per liter) i.e. 8 times that of cellulose
Pyridine	95 ml.	

TABLE 35

Combined Iodine and Sulfur Analyses on Tosylated Cellulose Followed by Iodination

Series DT Wetted made at Different Temperatures

(1) Wetting Temperature	No wetting	0°	25±0.1°	50±2°	75±2°	steam
(2) I%	3.08	3.57	3.73	3.64	3.78	3.12
(3) S%	0.456	0.466	0.578	0.606	0.441	0.475
(4) Calculated Primary OH Substituted per G.U.	0.0414	0.0487	0.0506	0.0496	0.0510	0.0420
(5) Calculated Free Primary OH per G.U.	0.9586	0.9513	0.9494	0.9504	0.9490	0.9580
(6) Calculated Secondary OH Substituted per G.U.	0.0248	0.0249	0.0311	0.0326	0.0236	0.0253
(7) Calculated Free Secondary OH per G.U.	1.9752	1.9751	1.9689	1.9674	1.9764	1.9747

substitution at the secondary positions. In general, the following features can be observed (Fig. 17, p. 113). At 25°, the wetting and drying process tends to facilitate the overall degree of nitration but shows a gradual decline of the total degree of tosylation, this contrast might be accounted for by their different modes of reaction just mentioned. As for the two positions, primary hydroxyls are more easily nitrated but more resistant to tosylation as the cycles proceed. On the other hand, the secondary hydroxyls tend to decrease in their reactivities toward both reagents.

Similarly, Table 37 (p.112) summarizes the results for cycle 1 of series T and III-DT with the only difference that column 1 indicates the wetting temperatures instead of cycles. The overall degree of nitration increases gradually from 0° onward until up to steam wetting which causes a general collapse of the sample (Fig. 18, p. 114). The total degree of tosylation shows a decline, in general, as the wetting temperature increases. The reactivity of the primary hydroxyls is somewhat greater between the temperature range 25° - 75° than the two extremities of 0° and in steam. The trend is less significant at the secondary positions though it is interesting to point out that whenever its accessibility (the secondary) is relatively increased or decreased shown by the degree of nitration, the same is noted with the degree of tosylation (compare the corresponding figures in columns 6 and 7 of Table 37 on p.112). This oberservation may be more than coincidental.

TABLE 36

Comparison of Nitration and Tosylation -Iodination Data - on Cellulose Wetted at 25°[a]

(1) Wetting Cycle	0	1	5	11	15
(2) Total Hydroxyls Nitrated	1.799	1.781	1.807	1.839	1.842
(3) Total Hydroxyls Tosylated	0.146	0.141	0.130	0.148	1.122
(4) Primary[b] Hydroxyls Nitrated	0.3167	0.3813	0.4421	0.5054	0.5231
(5) Primary[c] Hydroxyls Tosylated	0.0875	0.0925	0.0826	0.0805	0.0642
(6) Secondary Hydroxyls Nitrated	1.432	1.400	1.355	1.334	1.316
(7) Secondary Hydroxyls Tosylated	0.0517	0.0495	0.0471	0.0565	0.0465

[a] Nitration was carried out on Cellulose samples Series I and tosylation on Series II

[b] Columns (4) and (6) are taken from Tables 24 and 25 (both 3rd column p.90)

[c] Columns (5) and (7) are taken from Columns (4) and (6) of Table 33 on p.104)

TABLE 37

Comparison of Nitration and Tosylation - Iodination Data on Cellulose Wetted Once at Different Temperatures[a]

(1) Wetting Temperature	No Wetting	0°	25°	50°	75°	steam
(2) Total Hydroxyls Nitrated	1.799	1.758	1.781	1.812	1.871	1.793
(3) Total Hydroxyls Tosylated	0.0679	0.0864	0.0897	0.0864	0.0857	0.0730
(4) Primary[b] Hydroxyls Nitrated	0.3167	0.4303	0.3813	0.3688	0.5190	0.4197
(5) Primary[c] Hydroxyls Tosylated	0.0414	0.0432	0.0506	0.0496	0.0510	0.0420
(6) Secondary Hydroxyls Nitrated	1.482	1.328	1.400	1.443	1.352	1.374
(7) Secondary Hydroxyls Tosylated	0.0248	0.0249	0.0311	0.0326	0.0236	0.0253

[a] Nitration carried on Series T and Tosylation of Series III-DT

[b] Columns (4) and (6) taken from Table 24 and 25 (p. 90)

[c] Columns (5) and (7) taken from Columns (4) and (6) of Table 35 on p.109.

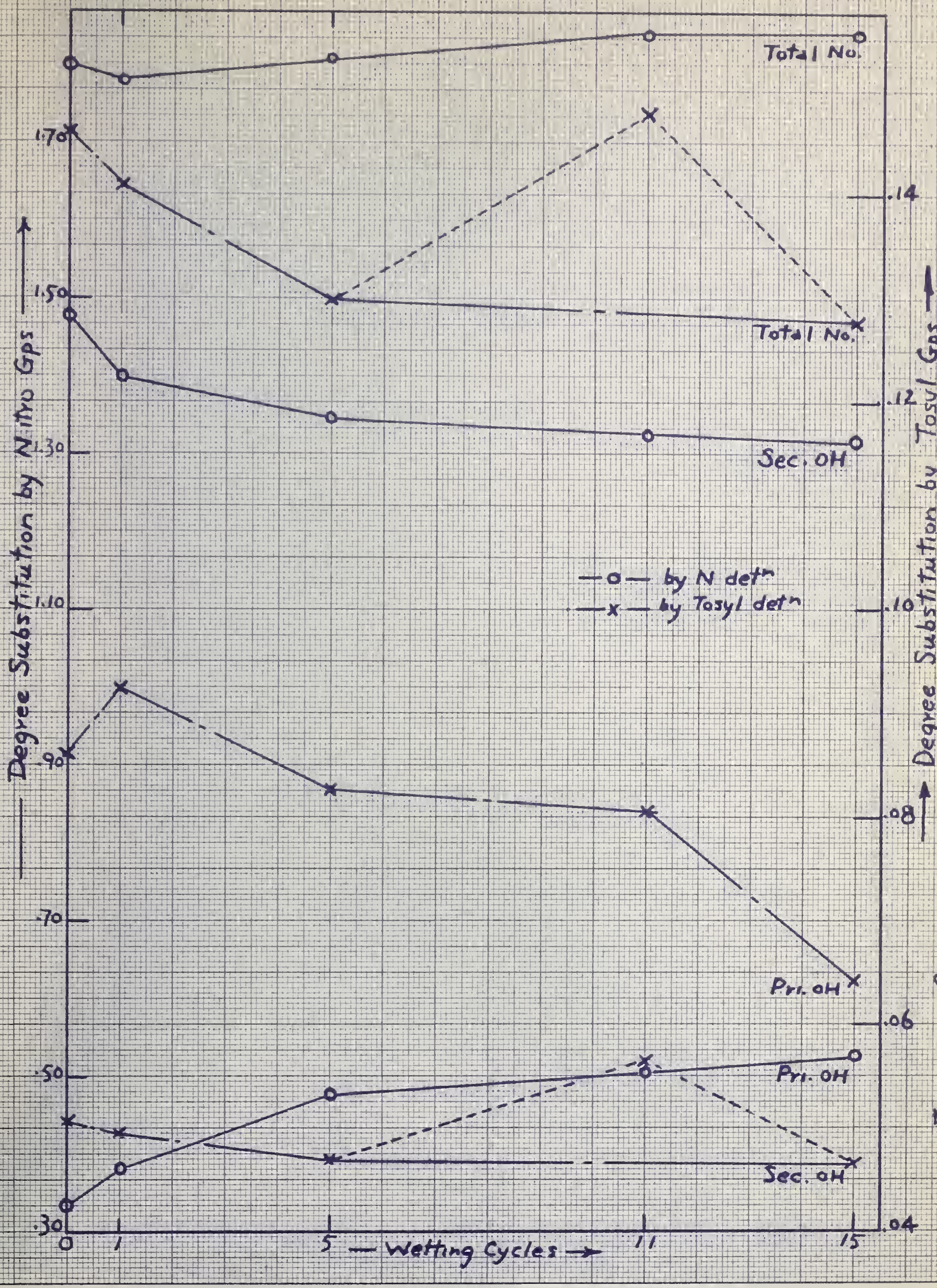


Fig. 17 Comparison of data obtained from nitration and tosylation-iodination of series wetted at 25°

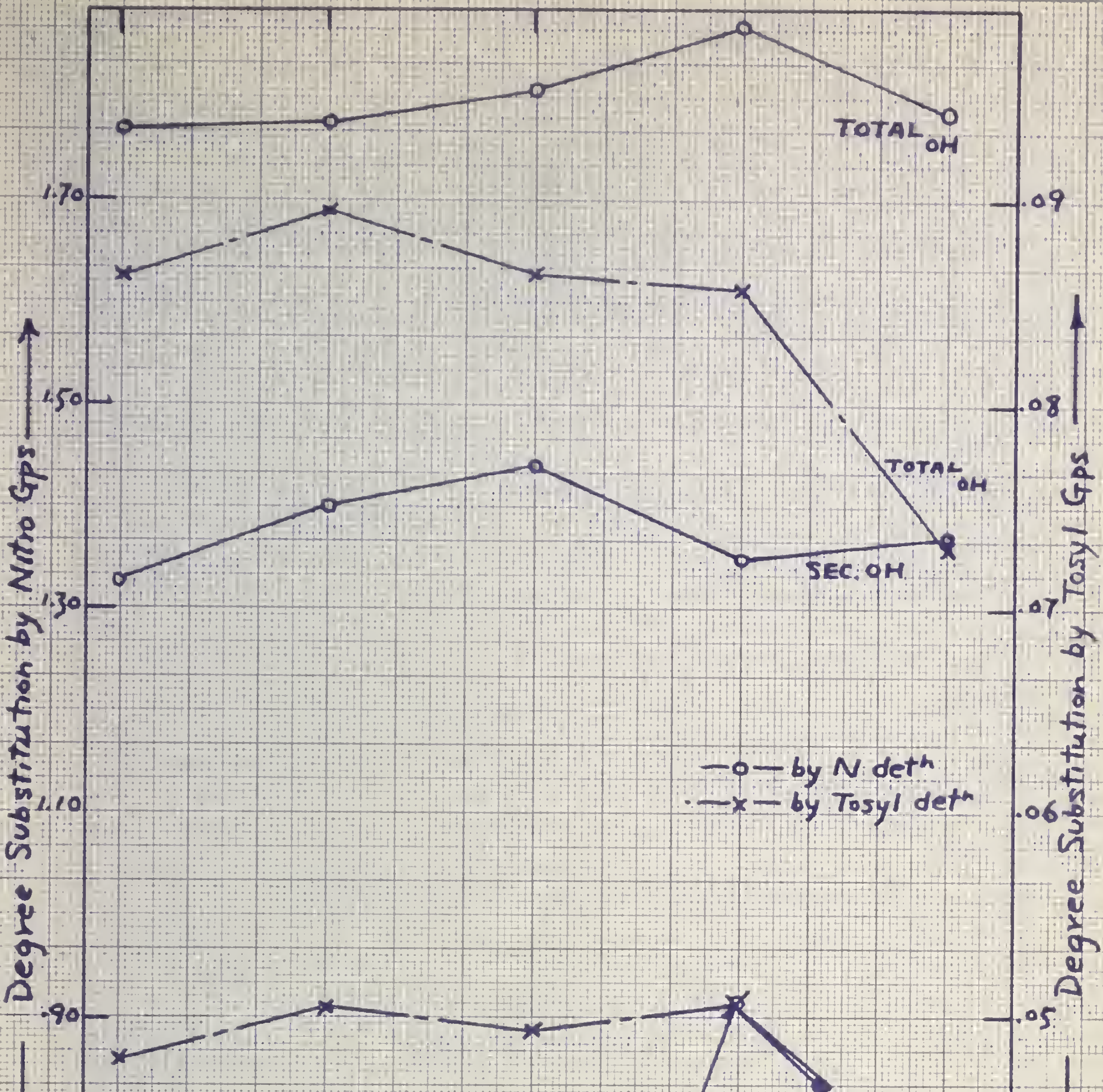


Fig. 18 Comparison of data obtained from nitration and tosylation-iodination of samples wetted at different temperatures

In general, the results of this project as a whole support the hypothesis that previous moisture history plays an important role in influencing the accessibilities of the cotton linters toward nitrating mixture and tosyl chloride. To summarize the data more specifically, the following conclusions can be noted:

1. Repeated wetting at 0° and 25° tends to facilitate the accessibility of the primary hydroxyls of the dried cotton linters toward nitration. Repeated wetting at 50°, 75° and in steam results in a reverse trend.
2. Repeated wetting at 0° tends to increase the reactivity of the secondary hydroxyls of the dried cotton linters toward nitration. Repeated wetting at 25°, 50°, 75° and in steam shows an opposite trend.
3. Both the primary and secondary hydroxyls of the alternately wetted (at 25°) and dried cellulose samples decrease gradually in their accessibilities toward tosyl chloride.
4. There seems to exist an optimum wetting temperature (around 25°) at which both the primary and secondary hydroxyls possess maximum reactivity toward tosyl chloride.
5. Support is given for the concept of homogeneous reaction during nitration.

BIBLIOGRAPHY

1. Rosenthal, A. and Brown, R.K. Pulp and Paper Mag. Can. 51 (6): 1950, p.99.
2. Brickman, W. J., et al. Can. J. Chem. 31: 1953, p. 550-563.
3. Rosenthal, A., Thesis submitted to the Committee on Graduate Studies ~~s~~ of University of Alberta, 1949, in partial fulfilment of the requirements for the Degree of Master of Science, p. 21-22.
4. Brown, R.K., Thesis submitted to the Faculty of Graduate Studies of McGill University, 1946, in partial fulfilment for the Degree of Doctor of Philosophy. p. 84-87.
5. Ott, E. and Spurlin, H. M. 'Cellulose and Cellulose Derivatives", Interscience Publishers Inc., N.Y., Second Edition, 1954, p. 5-12.
6. Nickerson, R. F. and Habrle, J.A., Ind. Eng. Chem. V. 38, 1946, - p. 299-301.
7. Berkley, E. E. and Kerr, T., Ind. Eng. Chem. V 38, 1946, p. 304
8. See ref. 5, p. 236 - 243.
9. Mark, H., Chem. Revs., 26, 1940, p. 169.
10. Katz, J.R., Trans. Faraday Soc., 29, 1933, p. 279.
11. See ref. 5, p. 270
12. Frilette, V. J., Hanle, J. and Mark, H., J. Amer. Chem. Soc. 70, 1948, p. 1107.
13. Legrand, C. and Champetier, S., J. Polymer Sci., 10, 1953, p. 223.
14. Assaf, A.G., Haas, R.H. and Purves, C.B., J. Amer. Chem. Soc. 66, 1944, p. 66.

15. Kollmann, F., Naturwissenschaften, 32, 1945, p. 121 - 138. c.f. C.A. 40, 1946, 2297.

16. Schur, M.O. and Hoos, B.G., Ind. Eng. Chem., 29, 1937. p. 26.

17. Bletzenger, J.C., Ind. Eng. Chem., 35, 1943, p. 474.

18. Treiber, E., Svensk Paperstidn, 58, 1955, p. 185-195. c.f. C.A. vol. 5, 1956. 3755.

19. De Croes, G. C. and Tamblyn, J.W., Modern Plastics 29, No. 8, 1952, p. 127-136.

20. Badley, W., Frilette, V. J. and Mark, H., Ind. Eng. Chem., 37, 1945, p. 227.

21. Berl, E., Ind. Eng. Chem., Anal. Ed., 13, 1941, p. 322.

22. See ref. 5, p. 729 - 730.

23. Dorée, C., 'The Methods of Cellulose Chemistry', Chapman and Hall, Ltd., London, 1943, p. 221 - 235.

24. Elving, P. J. and McElroy, W.R., Ind. Eng. Chem., Anal. Ed., 14, 1942, p. 84 - 88.

25. Cramer, F. B. and Purves, C.B., J. Amer. Chem. Soc., 61, 1939, p. 3458 and p. 3463.

26. Murray, G. E. and Purves, C. B., J. Amer. Chem. Soc., 62, 1940, p. 3194.

27. Hockett, F. B., Cramer, R.C. and Purves, C.B., J. Amer. Chem. Soc., 61, 1939, p. 3463.

28. Mahoney, J. F. and Purves, C. B., J. Amer. Chem. Soc., 64, 1942, p. 9.

29. See ref. 4, p. 100-111.

30. Heidt, L. J., Gladding, E. K. and Purves, C.B., Paper Trade Journal, 1945, p. 31-39; c.f. C.A. 40, 1946, 546.

31. See ref. 3, p. 58-59.

32. See ref. 5, p. 820-823.

33. Rigby, G.W., U.S. Patent 2,123,806; c.f. C.A. 32, 1938, 7263.

34. Oldham, J.W. and Rutherford, J.K., J. Amer. Chem. Soc.; 54, 1932, p.366.

35. Purves, C.B. and Gardner, T.S., J. Amer. Chem. Soc., 64, 1942, p. 1539.

36. Honeyman, J. Chem. Soc., 1947, p. 168.

37. Malm, C.J., Tanghe, L.J. and Laird, B.C., J. Amer. Chem. Soc., 70, 1948, p. 2740.

38. Heuser, E., Heath, M. and Shockley, M.H., J. Amer. Chem. Soc., 72, 1950, p. 670.

39. Parr Bomb Manual No. 116, Parr Instrument Co., Illinois, 1947.

40. Clark, E.P., 'Semimicro Quantitative Organic Analysis', Academic Press Inc., 1943, p. 61-62.

41. See ref. 3, p. 23-25.

42. Fieser, L.E., 'Experiments in Organic Chemistry', Second Ed., D.C. Heath and Co., N.Y., 1941, p. 359-360.

43. See ref. 4, p. 34-36.

44. Berl, E., Ind. Eng. Chem., Anal. Ed., 13, 1941, p. 322.

45. Wiggam, D.R., J. Phys. Chem., 35, 1931, p. 536.

46. Sanderson, R.T., 'Vacuum Manipulation of volatile compounds', John Wiley and Sons, Inc., N.Y., 1948, p. 8.

47. See ref. 42, p. 364.

48. Walton, H.F., ' Inorganic Preparations', Prentice-Hall 1953, p. 138.

49. Ewing, G.W., 'Instrumental Methods of Chemical Analysis', McGraw-Hill Book Co., Ltd., 1954, p. 80.

50. Brown, R.L., and Purves, C.B., Pulp and Paper Mag. Can. 48(6), 1947, p. 100.

51. Stamm, A.J. and Tarkow, H., J. Phys. and Colloid Chem. 54, 1950, p. 745.

52. See ref. 3, p. 89-94.

53. See ref. 4, p. 108-110.

54. See ref. 5, p. 723.

55. Mahoney, J.F. and Purves, C.B., J. Amer. Chem. Soc., 64, 1942, p. 15.

56. See ref. 5, p. 734 - 735.

57. Timell, T.E., Chem. & Eng. News. Sept. 26, 1955, p. 4036.

58. Tipson, S. Clapp, M.A. and Cretcher, L.H., J. Org. Chem. 12, 1947, p. 133.

59. Hockett, F.E. and et al, J. Amer. Chem. Soc. 68, 1946, p. 927.

60. See ref. 3, p. 35-45.

61. See ref. 49, p. 362 - 364.

62. Kolthoff, I.M. and Sandell, E. B., 'Text Book of Quantitative Inorganic Analysis', The MacMillan Co. N.Y., Third Edition, 1953, p. 308.

63. Reeves, R.E., J. Amer. Chem. Soc., 76, 1954 p. 4595; 71, 1949, p. 215; 72, 1950, p. 1499.

B29775